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Laboratory concentration of a lead-zinc-fluorspar ore from southern Illinois

Shiou-chuan Sun

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LABORATORY CONCENTRATION OF A LEAD-ZINC-FLUORSPAR
ORE FROM SOUTHERN ILLINOIS.

- By -

Shiou - Chuan Sun.

A

T H E S I S

submitted to the Faculty of the

SCHOOL OF MINES AND METALLURGY

OF THE UNIVERSITY OF MISSOURI,

in partial fulfillment of the work required for the

D E G R E E   O F

Master of Science in Mining and Metallurgy.

Rolla, Missouri.

1 9 3 8 .

Approved by ___*R B Cooke*___

Assistant Professor of Metallurgy and Ore Dressing.

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LABORATORY CONCENTRATION OF A LEAD-ZINC-FLUORSPAR
ORE FROM SOUTHERN ILLINOIS.

- By -

Shiou-Chuan Sun.

PREFACE.

This thesis is presented to the Faculty of
the School of Mines and Metallurgy of the University
of Missouri in partial fulfillment of the work re-
quired for the degree of Master of Science in Mining
and Metallurgy.

The results of the investigation herein
embodied were obtained from work carried on in the
Metallurgy Department of the Missouri School of Mines
and Metallurgy.

ACKNOWLEDGMENTS.

The writer wishes to express his obligations
to Dr. S.R.B. Cooke, Assistant Professor of Metallurgy
and Ore Dressing of the School of Mines and Metallurgy
of the University of Missouri for his instruction and
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the Mining Department; and to Professor Chas. Y.
Clayton, Head of the Metallurgical Department of the
same school, who encouraged, guided and advised the
writer; and to Professor Herbert R. Hanley, Professor

of Metallurgy at the Missouri School of Mines and Metallurgy, whose suggestions with regard to the chemical analyses conducted by the writer were highly appreciated.

OBJECT.

The purpose of this investigation was to ascertain the feasibility of preparing marketable products from a rather complex sulphide-fluorspar ore.

SCOPE OF WORK DONE.

The ore was examined exhaustively by chemical, microscopic, and mineralogical methods of analysis. After a thorough knowledge of the physicl characteristics of the ore had been obtained, flotation concentration tests were made to separate the sulfide minerals from the fluorspar and to attempt to prepare lead-zinc and fluorspar concentrates of marketable grade.

Introduction

(I). <u>Location of the Ore</u> :-

The ore investigated comes from the Cave-in-Rock district of Southern Illinois.

(II). <u>History of Fluorspar-Zinc-Lead Ore in Southern Illinois</u>

Lead and zinc mining in Southern Illinois commenced about 1842. At that time fluorspar had no commercial value, and it was not until about 1870 that the first shipment of fluorspar was made from this district. Since then, the fluorspar has been a constant product, as well as minor quantities of zinc and lead.

The use of fluorspar as a flux in the basic open-hearth steel process started about 1898, and the rapid development of that process created an increased demand for the mineral. Mining on a fairly large scale started about 1910, when systematic methods of mining and milling were developed.

(III). Uses of the Ore :

As the ore contains fluorspar, zinc and lead, it may be briefly discussed as follows:

(A). Uses of lead: Lead is one of the six so-called pre-historic metals. The oldest piece of lead extant is probably that of a figure in the British Museum which antedates 380 B.C. From ancient times until the present lead has become increasingly important in industrial uses. The following table shows the use of lead in the United States for 1936.

Table (I). Use of Lead in the United States.
(Thousands of Short Tons 2000#)*

Purpose	Thousands of short tons(1936)
White Lead	85.5
Red Lead & PbO	54.0
Storage Battery	191.0
Cable Covering	64.4
Building	40.0
Automobile	11.0
Railway Equipment	2.4
Ship Building	0.2
Ammunition	32.5
Terne Plate	6.2
Foil	28.5
Bearing Metal	16.5
Solder	22.0
Type Metal	17.0
Calking	13.5
Casting	5.7
Other Uses	133.0
Total	725.4

*Herbert R. Hanley, Lecture Sheet of Lead Metallurgy. Missouri School of Mines, Rolla, Mo. 1937, p.3

(B). **Uses of Zinc:** Recognition of zinc as a separate metal is uncertain prior to 1509 A.D.. P. Neogi[a] has stated that zinc was produced as a separate metal in India as early as the seventh century. R.T. Chang[s] states that zinc was similarly produced in China as early as the eleventh century. Table (II) shows the consumption of zinc in the United States for the year 1932.

Table (II) - **Use of Zinc in United States** (1932).

Purposes	Thousands of Short Tons (2000#)	Percentages
Galvanized	109	40.8
Sheets	32.5	----
Tubes	16.0	----
Wire	12.1	----
Wire Cloth	4.4	----
Shapes	24.0	----
Brass Making	66.0	24.7
Rolled Zn	48.0	17.9
Die Casting	17.0	6.4
Other Purposes	27.0	----
Total	376.0	100.0

[a] Read, T.T.; "Role of Mining in the Development of Civilization" - Eng. & Min. Journal; #12, December 1932. McGraw-Hill Book Company, New York City.

[s] Chang, R.T.; Eng. & Min. Journal, #2, February, 1932. McGraw-Hill Book Company, New York City.

[4] Hanley, H.R.; Lecture Sheet of Zinc Metallurgy, p. 7, 1937. Missouri School of Mines, Rolla, Mo.

(C) **Uses of Fluorspar:** Fluorspar is used as a flux and cleansing agent in the basic open-hearth steel process and in the manufacture of hydrofluoric acid, artificial cryolite, ceramic products, such as opalescent glass, enamel and sanitary ware, vitrolite, etc. The steel industries consume about 85% of the fluorspar produced and the remaining 15% is used by the other industries cited above. The steel industry demands a gravel spar having an analysis of about 85% calcium fluoride and not over 5% silica. The ceramic grade is a ground fluorspar containing 96 to 98% calcium fluoride and 1.5 to 2.5% silica. The acid grade has an analysis of 98 calcium fluoride and not over 1% silica, and is shipped in both fine and lump form.

(IV). **Geology of the Ore Deposit.**

The rock formations of the Southern-Illinois fluorspar-zinc-lead ore district are of Devonian, Mississippian, and Pennsylvanian age and consist of shales, sandstones and limestones. The Mississippian series predominate, while the Pennsylvanian rocks are found only on the higher ridges or where extensive faulting has brought them into juxtaposition with the older formation.

The rook formations are approximately horisontal with local dips and are faulted very extensively into irregular blocks. A few igneous dikes, sills, and plugs are to be found in the district.

The fults are all normal faults, no thrust faults having been identified. The faulting results from extensive doming, caused possibly by deep seated igneous intrusion followed by collapse or re-adjustment of the surface after the settling of the igneous mass. The mineralised veins commonly occupy the faults, though some mineralisation has taken p,ace along fractures where there has been no dislocation. In the vicinity of Cave-in-Rock, a commercial ore deposit occurs in a blanket formation resulting from replacement of limestone. A cross section of the main faults in Southern Illinois is shown in Figure I. This figure can represent all the geological conditions in the district of Southern Illinois.

(V). <u>General Methods Used in Mining Fluorspar-Zinc-</u>

<u>Lead Ores in Southern Illinois.</u>

Cronk, A.H.; "Underground Mining Practice and Costs of a Fluorspar Mine at Rosiclare, Illinois." I.C. 6384. Dec. 1930, U.S. Bureau of Mines, p.2.

6 ibid. p.2.

-7-

www.manaraa.com
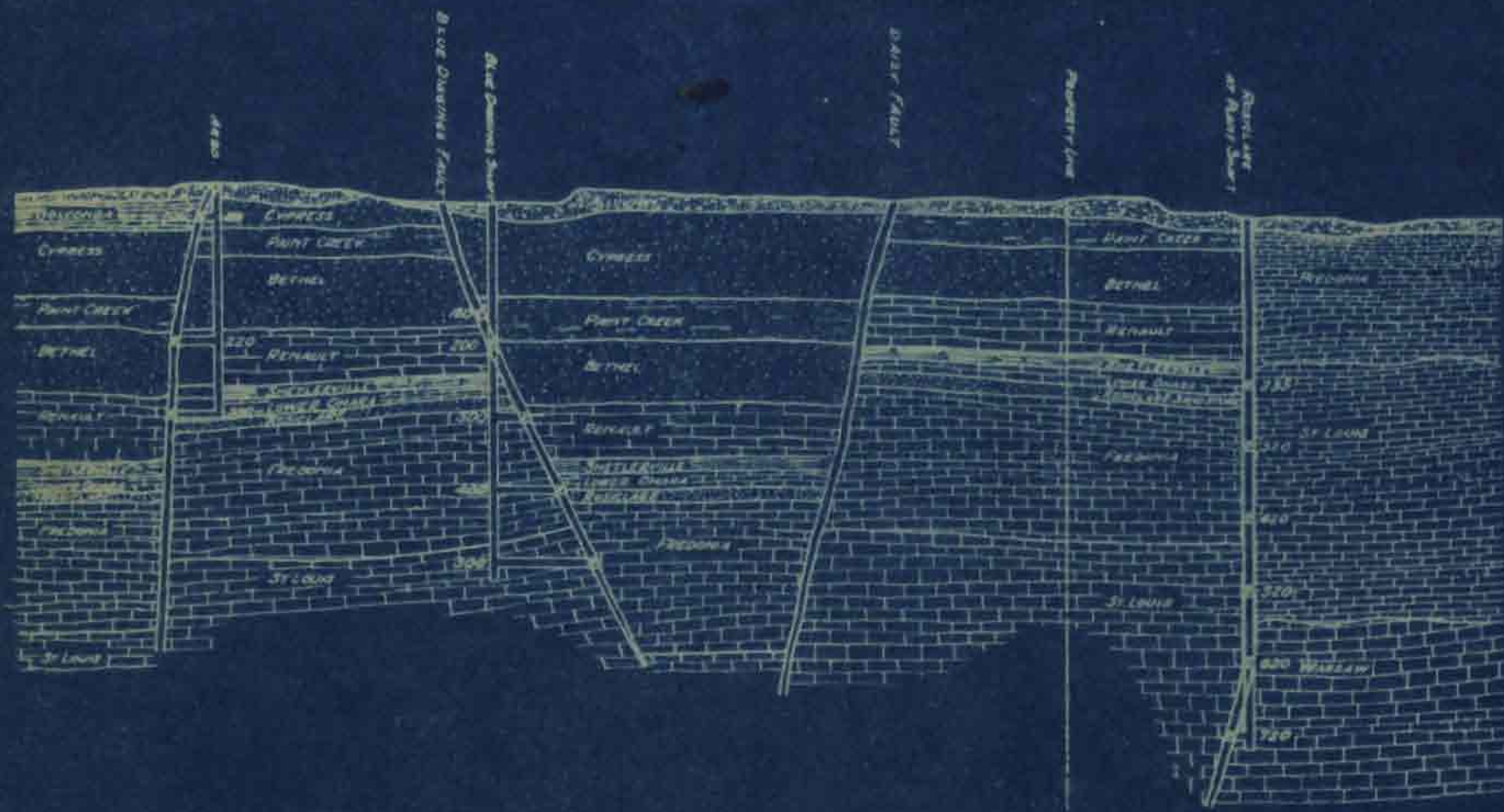
Figure I.- Ideal cross section through Rosiclare, Daisy, Blue Diggings, and Argo faults
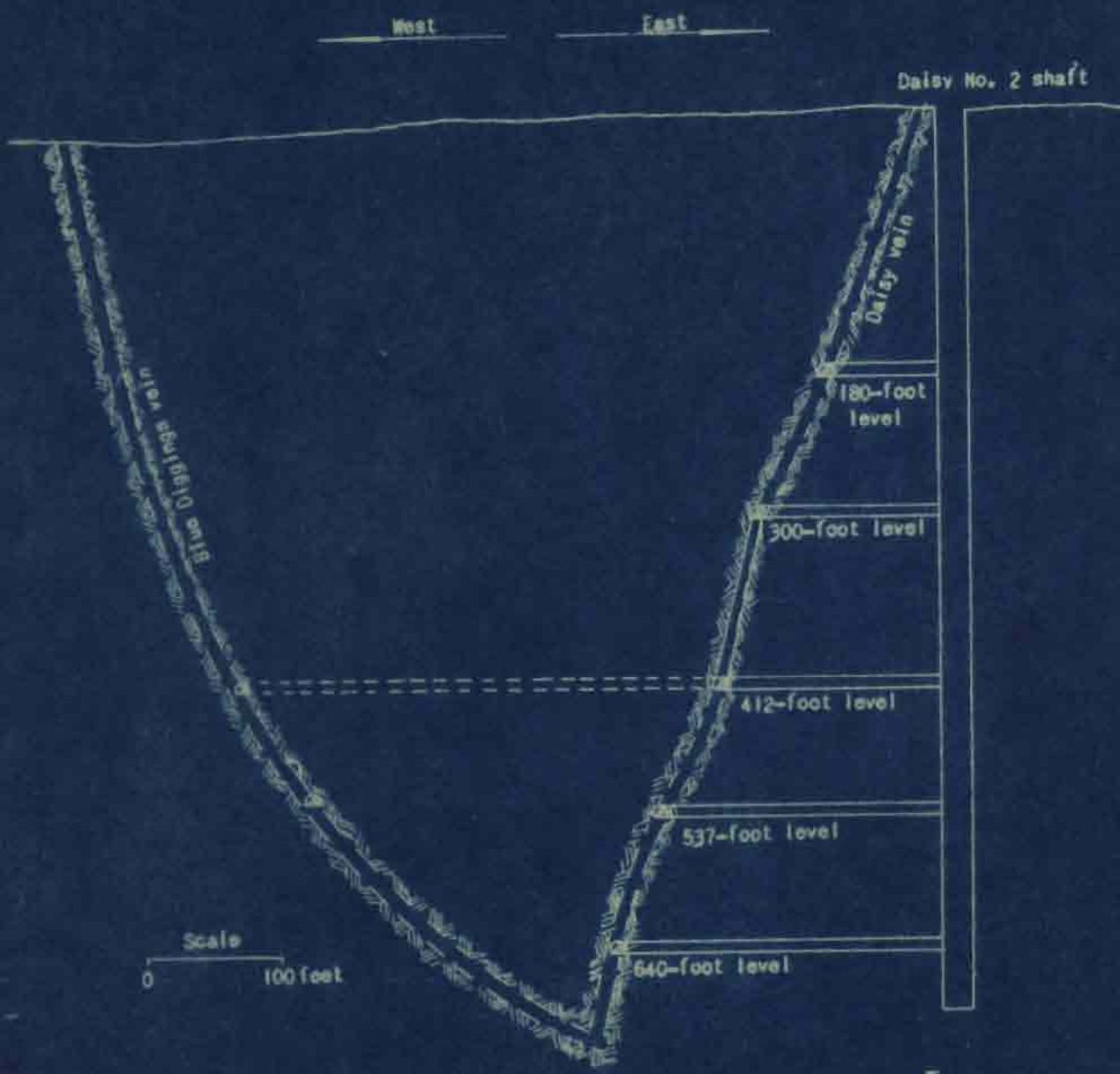
Figure 2.- Ideal vertical section through Daisy and Blue Diggings veins at No. 2 shaft

West   East

Daisy No. 2 shaft

Daisy vein

Blue Diggings vein

180-foot level

300-foot level

412-foot level

537-foot level

640-foot level

Scale
0   100 feet
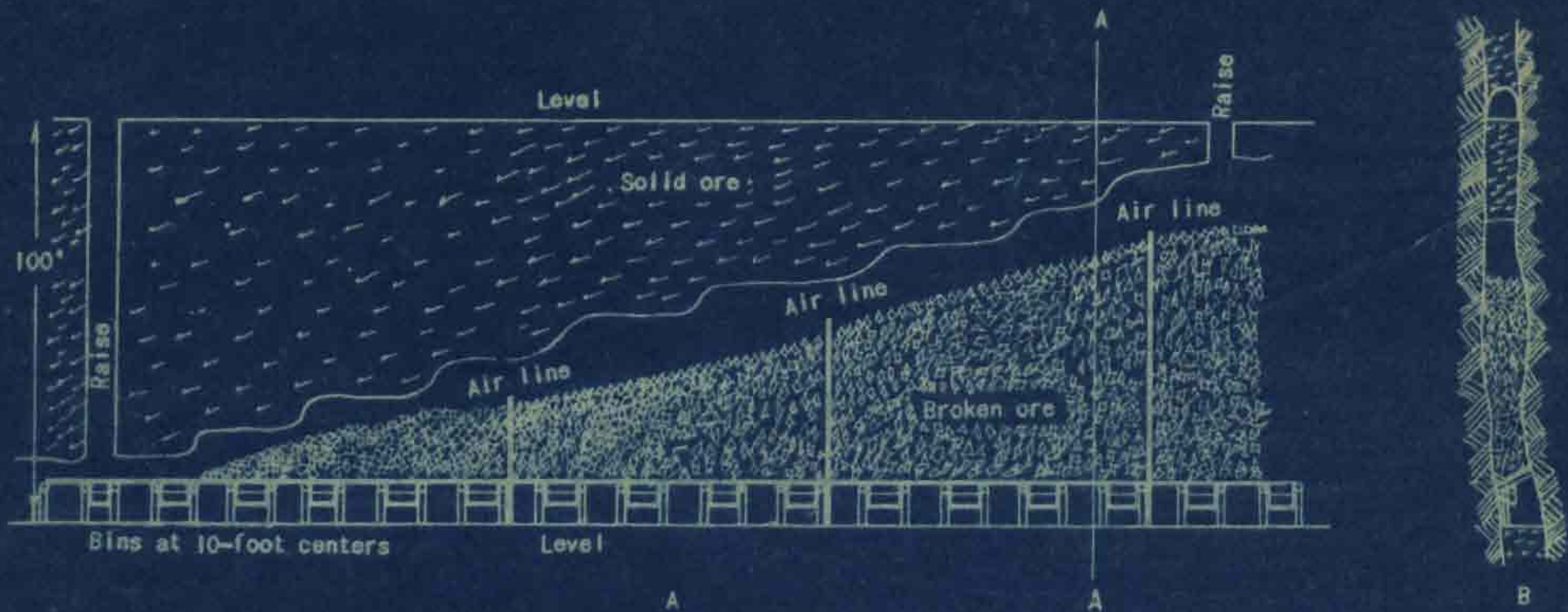
Figure 3.— Typical shrinkage stope: A, Longitudinal section; B, cross section

The mining method is simple; shallow vertical shafts are sunk to the center or to the side of the ore body, from which the ore is reached by cross-cuts. Fig. (2) shows the general manner of development in these mines. The typical mining method used in this district is shrinkage stoping, which is shown in Fig.(4).
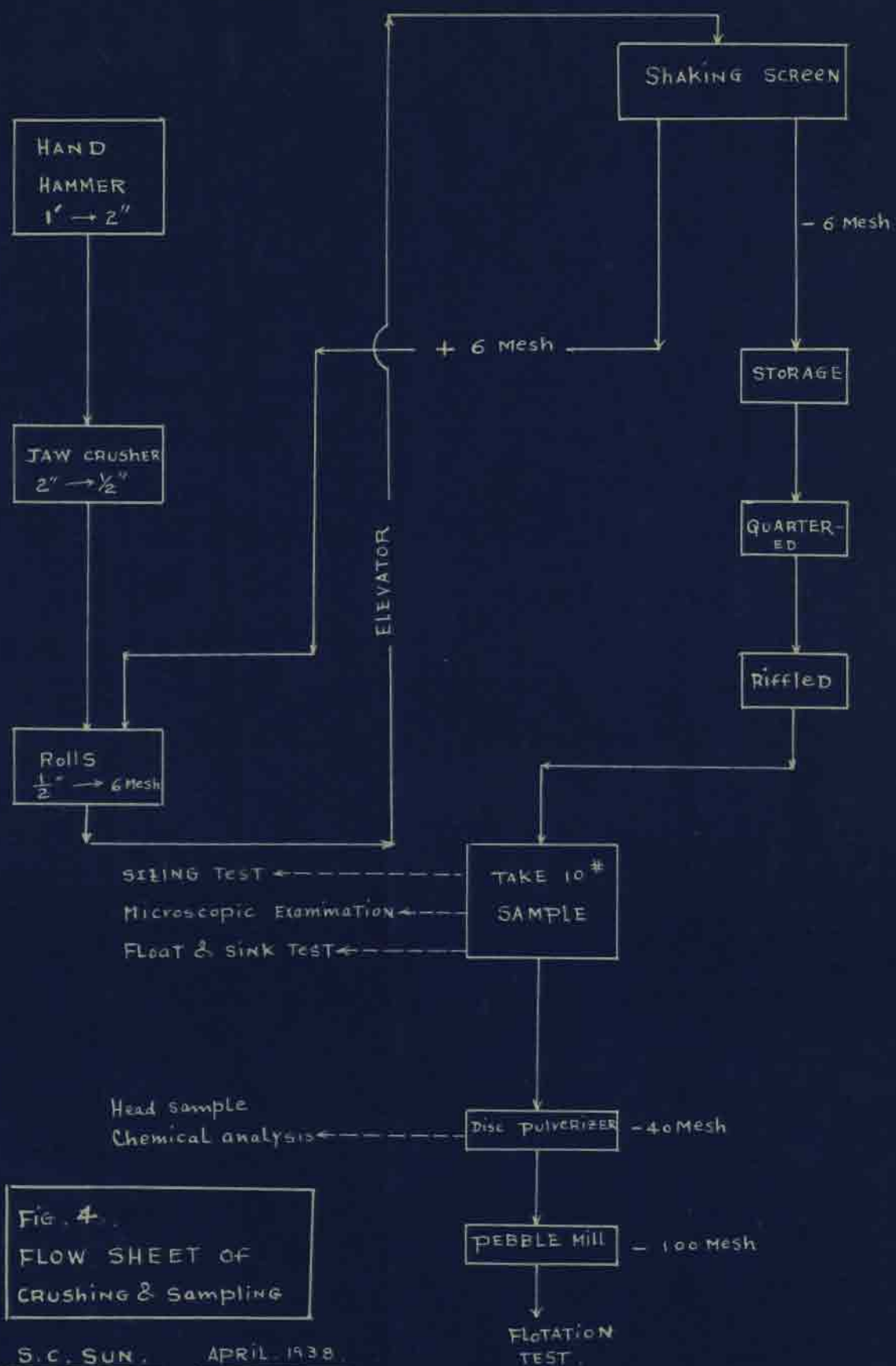
FIG. 4.
FLOW SHEET OF
CRUSHING & SAMPLING

S.C. SUN.   APRIL 1938.

CHAPTER ONE

"Sampling and Screen Analysis"

"Preparation of Ore Sample for Screen Analysis"

(A) Crushing :-

Ore invariably comes from the mine in lumps
which are unfitted for any kind of concentration other
than hand sorting. Crushing is always a part of all
flow sheets. Since the method of crushing, at least
in large sizes, has little or no effect on the char-
acter of the subsequent mill process, the flow sheet
of the crushing system may be studied without regard
to the mineral content of ore.

The ore, as received, was in lump form. The
larger pieces from six inches to one foot in size
were spalled down to two or three inches to give a
feed suitable for the small laboratory jaw crushers.

The jaw crusher was used for coarse crush-
ing to reduce the particles from three or two inches
to 1|4 inch or finer in size. Rolls were used for
finer crushing, an electrically driven shaking screen

(6 mesh), being in closed circuit with the rolls.[7]

After roll crushing, the ore was thoroughly mixed and quartered and a portion of ten pounds was obtained by a succession of passes through a Jones riffle. This sample was used directly for sizing tests, microscopic examination, and float- and sink testing. For chemical analysis and flotation tests, fine sizes are required and the roll-crushed head sample was ground by a disc pulveriser to pass 40 mesh, then by a pebble mill through 100 mesh. Fig. (Ia) shows the procedure adopted.

(II) Screen Analysis of Ore Sample

In ore testing of any kind a screen analysis of the head sample is usually made. Taggart[8] defines the various type of sizing tests as follows:

---

[7] All sizes referred to in this paper are in terms of the Tyler Standard Screen Scale.

[8] Taggart, A.F., "Handbook of Ore-Dressing" John Wiley & Sons, Incorporated, 1927 page 1181.

"Sizing analysis consists in quantitative separation of a mass of material of various sizes into a number of grades, each characterized by relatively small size intervals between largest and smallest particles. The means of grading are (a) screening and (b) settling in a fluid, usually water. Screen grading, used on granular material, is called screen analysis; grading by settling in fluids, used for the finest sizes, is called elutriation. Frequently the various grades are assayed, in which case the operation is called sizing-assay-test."

A sizing-assay test does not necessarily involve chemical analysis of the products, as sink-and-float estimation of the valuable mineral content may suffice.

Screen analyses, without assays, are applied principally to the study and control of particle-size distributions in the products of crushing and grinding.

Sizing-assay tests are used to ascertain the distribution of valuable minerals in the various sizes and, when supplemented by microscopic observation, to determine the degree of comminution nec-

essary to liberate the minerals from each other.
Hence such a test will determine to what extent
gravity concentration may be applied to a given ore
and how fine the ore must be ground to prepare it
for gravity concentration.

A sizing-assay test is applied only to
those ores that, by microscopic or low power micro-
scopic examination, are known to contain considerable
proportions of mineral particles larger than 200
mesh in diameter, thereby indicating that a suffi-
cient quantity of such particles may be separated by
methods other than flotation.

(B) <u>Sizing Analysis of Lead-Zinc-Fluor-
spar Ore</u>:

The ten pound sample obtained from the
crushed ore as explained on page (14) was too large
for a screen analysis, so it was reduced to about
2000 grams by careful coning and quartering. A
single Tyler screen analysis of this 2000 gram sam-
ple was made, and the results are presented in
Table (III).

Table (III). Screen Analysis of Sulphide-Fluorspar
Ore Crushed Through 6 Mesh.

No. Mesh	% of Weight	% Cumulative Weight
+ 10	11.80	11.80
+ 14	14.70	26.50
+ 20	11.85	38.55
+ 35	23.00	61.35
+ 48	14.10	75.45
+ 65	9.24	84.69
+100	7.31	92.00
+150	2.92	94.92
+200	2.12	97.04
-200	2.96	100.00
Total	100.00	

The data in Table (III) have been plotted
on a cumulative direct diagram and on a cumulative
logarithmic diagram, shown in Figures 3A and 3B
respectively.

The screen analysis appears to be normal
on account of the rather careful stage crushing
there is but a small amount of minus 200 mesh
material in the sample.

Plotting Curves :-

Of the several available methods for plot-
ting screen analyses the "cumulative direct plot"and
the "cumulative logarithmic plot" are the two most
valuable and generally used. The curves in either
case are plotted by marking the cumulative percent-
age of the material which remains on the sieves on
the corresponding vertical lines drawn from the
several openings on the horizontal scale of the dia-
gram. After drawing in the curve, the percentage
remaining on any set of openings other than those of
the testing sieves used, can be found by interpola-
tion, and in this way the re-distribution of the same
material by any assumed set of openings can be deter-
mined. The difference between a direct and logarith-
mic diagram is that in a direct plot the sieve open-
ings are laid out to an arithmetical scale, while in
the logarithmic plot they are laid down to a logari-
thmic scale. The pecularity of the arithmetical
scale is that the actual horizontal distances
between each vertical line increase or decrease in
the same ratio as that in which the screen openings
do, and in the logarithmic scale, the screen openings
are plotted to the logarithm of the diameter of the

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The Tyler Standard Screen Scale

Cumulative Direct Diagram of Screen Analysis on Sample of Sulfide Fluorspor ore of S- Illinois

Name S. C. Sun.   Date May, 1938

FIGURE 4. A

CUMULATIVE PER CENT WEIGHT RETAINED

SCREEN SCALE   RATIO 1.414

SCREEN SCALE RATIO 1.414
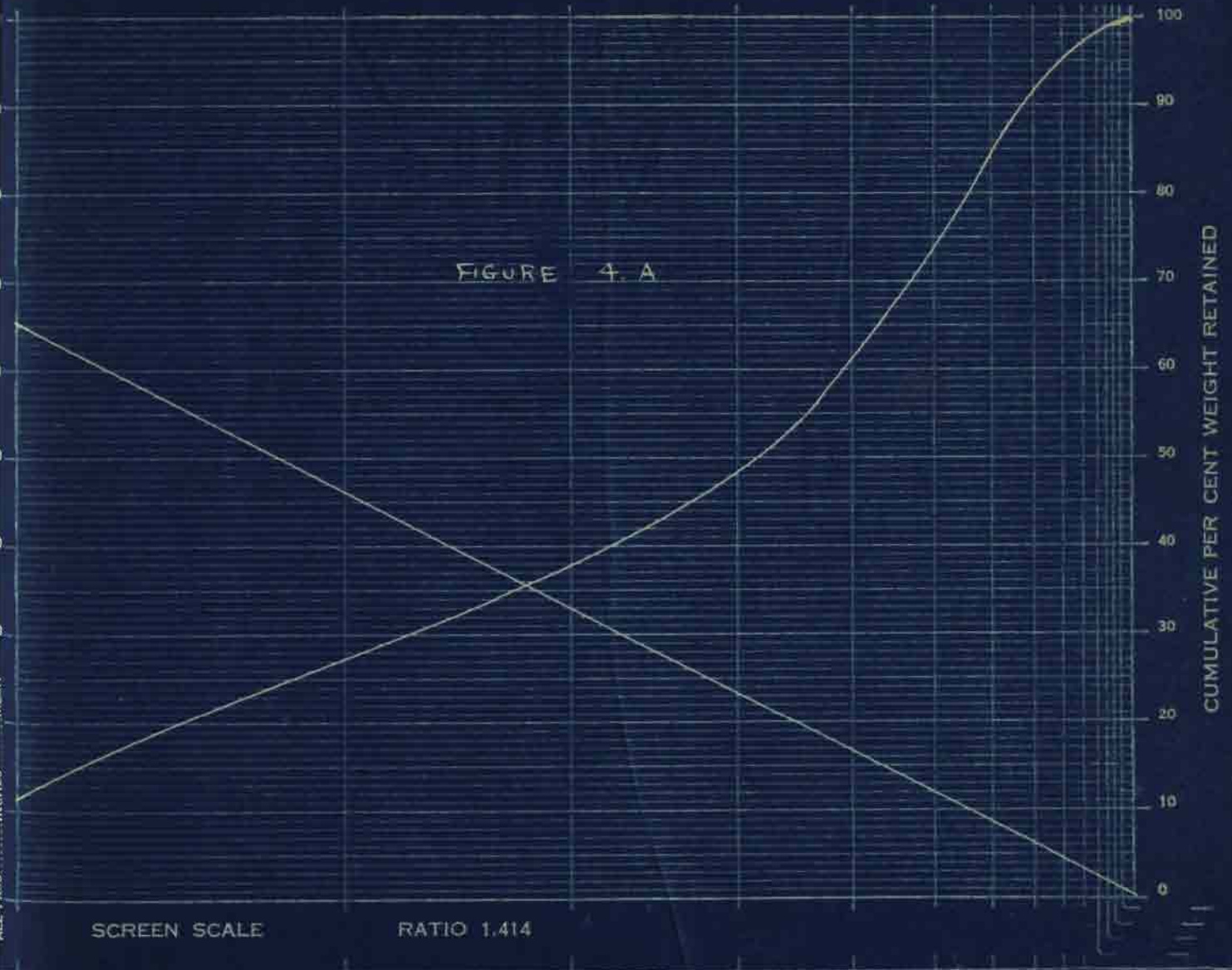
Locate the Screen passed through and also First Retaining Screen	Openings		Mesh	Diameter Wire Inches	Sample Weights	Per Cent	Per Cent Cumulative Weights						
	Inches	Milli-meters											
	1.050	26.67		.149									
	.742	18.85		.135									
	.525	13.33		.105									
	.371	9.423		.092									
	.263	6.680	3	.070									
	.185	4.699	4	.065									
	.131	3.327	6	.036									
	.093	2.362	8	.032									
	.065	1.651	10	.035	2.3?	11.8	11.80						
	.046	1.168	14	.025	2.99	14.7	26.50						
	.0328	.833	20	.0172	2.40	11.85	38.35						
	.0232	.589	28	.0125									
	.0164	.417	35	.0122	4.66	23.00	61.35						
	.0116	.295	48	.0092	2.85	14.10	75.45						
	.0082	.208	65	.0073	1.87	9.24	84.69						
	.0058	.147	100	.0042	1.49	7.31	92.00						
	.0041	.104	150	.0026	.99	1.42	94.42						
	.0029	.074	200	.0021	.43	2.11	97.04						
	.0029	.074	200	.0021	.66	2.96	100.00						
				Totals	20.24								

The Tyler Standard Screen Scale

Cumulative Logarithmic Diagram of Screen Analysis on Sample of Sulfide - fluorspar ore of S-Illinois

Name   Shiou chuan Sun   Date   March , 1938

FIGURE   4 B

SCREEN SCALE RATIO 1.414

Opening Millimeters	Opening Inches	Mesh	Diameter Wire Inches	Sample Weights	Per Cent	Per Cent Cumulative Weights
28.67	1.050		.149			
18.85	.742		.135			
13.33	.525		.105			
9.423	.371		.092			
6.680	.263	3	.070			
4.699	.185	4	.065			
3.327	.131	6	.036			
2.362	.093	8	.032			
1.651	.065	+ 10	.035	23.7	(1.8)	11.80
1.168	.046	+ 14	.025	29.7	14.7	26.50
.833	.0328	20	.0172	24.0	11.85	38.35
.589	.0232	28	.0125			
.417	.0164	35	.0122	46.6	23.00	61.35
.295	.0116	48	.0092	28.5	14.10	75.45
.208	.0082	65	.0072	18.7	9.24	84.69
.147	.0058	100	.0042	14.8	7.31	92.00
.104	.0041	150	.0026	5.5	2.72	94.72
.074	.0029	200	.0021	4.3	2.12	97.4
.074	.0029	300	.0021	4.0	2.16	100.00
		Totals		1924	100.00	

opening (the ratio between the sizes being a constant).
The horizontal scale of screen openings will be one
of equal spaces.

The direct-plotting is unique, all crush-
ing being expressed on diagrams of the same uniform
dimensions and having the same length of base line.
This renders comparison of the curves from various
crushings more comprehensive than when diagrams with
varying lengths of base line are used. The vertical
lines on the diagram represent any given set of sieve
openings having a constant ratio of $\sqrt{2}$. The first
left-hand vertical represents the screen opening
through which the sample has all been crushed. The
extreme right-hand vertical represents zero. A dia-
gonal drawn between these two points would be "the
line of perfect crushing", and the closer the plotted
curve approaches this diagonal line, the nearer the
actual crushing is to be ideal.

The logarithmic plot is a satisfactory way
to plot a curve, covering a wide range of sizes. By
using equal distances on the horizontal scale to
represent equal ratio of diameter, the curve for the
coarse sizes may be compressed and is extended for
the small sizes. The arithmetic difference between

the size of openings in the standard screen is small
for the fine sizes, while for the coarser screens the
arithmetic difference is greater. However the ratios
between the size of openings in successive sieves
are constant.

(C) <u>Purpose of Sizing Test</u> :-

(A) Through the study of sieve analysis of repre-
sentative samples, the crushing, pulverising
or screening operations can be maintained at
the highest possible efficiency.[9]

(B) To determine the work done in crushing:
Sieve analyses are the only means of finding
the ratio between the work done or energy ex-
pended, and the reduction in dimension that
results from the crushing process.

(C) Performance of screening equipment.

(D) Preparation of samples for subsequent tests.
(as float-and-sink; microscopic examination).

(E) Determination of the distribution of valuable
minerals in various sizes of particles.

---

[9] Catalogue 53, "The Profitable Use of Testing
Sieves." - The W.S. Tyler Company, Cleveland,
Ohio. pp. 6-7.

(F) Locating sieve openings other than those

used in the test.[10]

(G) Fineness tests in buying and selling.

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10   Catalogue 53, "The Profitable Use of Testing
      Sieves." - The W.S. Tyler Company, Cleveland,
      Ohio. pp. 30-31.

CHAPTER TWO

Mineralogical and Chemical Analysis of the Ore

(I) Mineralogy of the Ore.

A mineralogical examination of the coarse ore showed the presence of the following minerals:

> Sphalerite
> Galena
> Fluorite
> Calcite
> Chert
> Quartz

The sphalerite, fluorite, calcite and quartz are coarsely crystalline, much of the fluorite and quartz occurring as well developed crystals in cavities in the ore. Binocular microscope examination of the ore showed the presence of pyrite and of a small amount of chalcopyrite. A petrographic examination of some screen products showed that barite occurred in small amounts.

(II) Chemical Analysis of the Ore.

A quantitative chemical analysis gives more specific information concerning the elements present in an ore, but it does not give any clue to the actual mineral entities present. Hence chemical analysis and mineralogical analysis should go hand-in-hand when an ore is being investigated. A distinct disadvantage of mineralogical analyses

(whether by grain counts or by section methods) is the long time required.

The chemical analysis of the head sample of the ore is given in Table IV.

Table IV - Chemical Analysis of Sulphide
Fluorspar Ore
[11]

Substance	% Assay	Mineral Entity	% Mineral
Pb	2.12	PbS	2.45
Zn	15.3	ZnS	22.5
CaO	33.20	- - -	- - -
Insol(SiO_2)	22.3	SiO_2	22.3

The analysis of fluorspar is difficult, and in view of the lack of suitable equipment fluorine analyses were not made. The percentage of fluorite cannot be estimated from the lime analysis on account of the presence of calcium carbonate in the ore.

11   (1) Keffer, Robert; "Methods in Non-Ferrous Metallurgical Analysis" - McGraw-Hill Book Company, New York City, 1928.

(2) Willard & Furman; "Elementary Quanitative Analysis" - D. van Nostrand Company, New York City, 1936.

(III) Microscopic Examination of the Ore.

The mineralogical composition of the ore has been briefly mentioned at the beginning of this chapter. Several methods were used to examine the ore and the products obtained by treatment of the ore. These were:

(a) Float-and-sink tests.

(b) Microscopic examination. Examination by vertical illumination, transmitted light and by the binocular microscope were made.

(c) Photomicrographs were made of some of the ore samples.

(A) Float-and-Sink Tests

Principles: The media used for float-and-sink testing are heavy solutions which are lower in specific gravity than the sulphide minerals and higher in specific gravity than most of the gangue minerals. Therefore, if a mixture of sulphide and gangue minerals in a state of physical liberation, is placed in a heavy solution, the sulphides will sink and the gangue minerals will float. It is important to note the stipulation made above, that the minerals must be physically free. If interlocking occurs, the locked grains will either float or sink,

depending upon the relative proportion of the heavy
and light minerals present. It is obvious that this
method of analysis provides a powerful tool for
ascertaining:

(a) The size at which liberation of all minerals
occurs.

(b) The quantitative mineralogical analysis of
the ore and of products derived from it.

(c) Whether gravity concentration of the ore
is possible. Table (V) lists the specific
gravities of the mineral entities in the
Southern Illinois ore investigated.

Table (V) – Specific Gravities of the Minerals Occurr-
ing in Southern Illinois Sulphide-Fluor-
Spar Ore.

Minerals & Gangues	Sp.Gr.	Float-and-Sink
Quartz (SiO_2)	2.65	Float
Chert	2.68	
Calcite ($CaCO_3$)	2.72	
Fluorspar (CaF_2)	3.0-3.2	
Sphalerite (ZnS)	3.9-4.2	
Barite ($BaSO_4$)	4.3-4.7	Sink
Pyrite (FeS_2)	4.9-5.2	
Galena (PbS)	7.6-7.3	
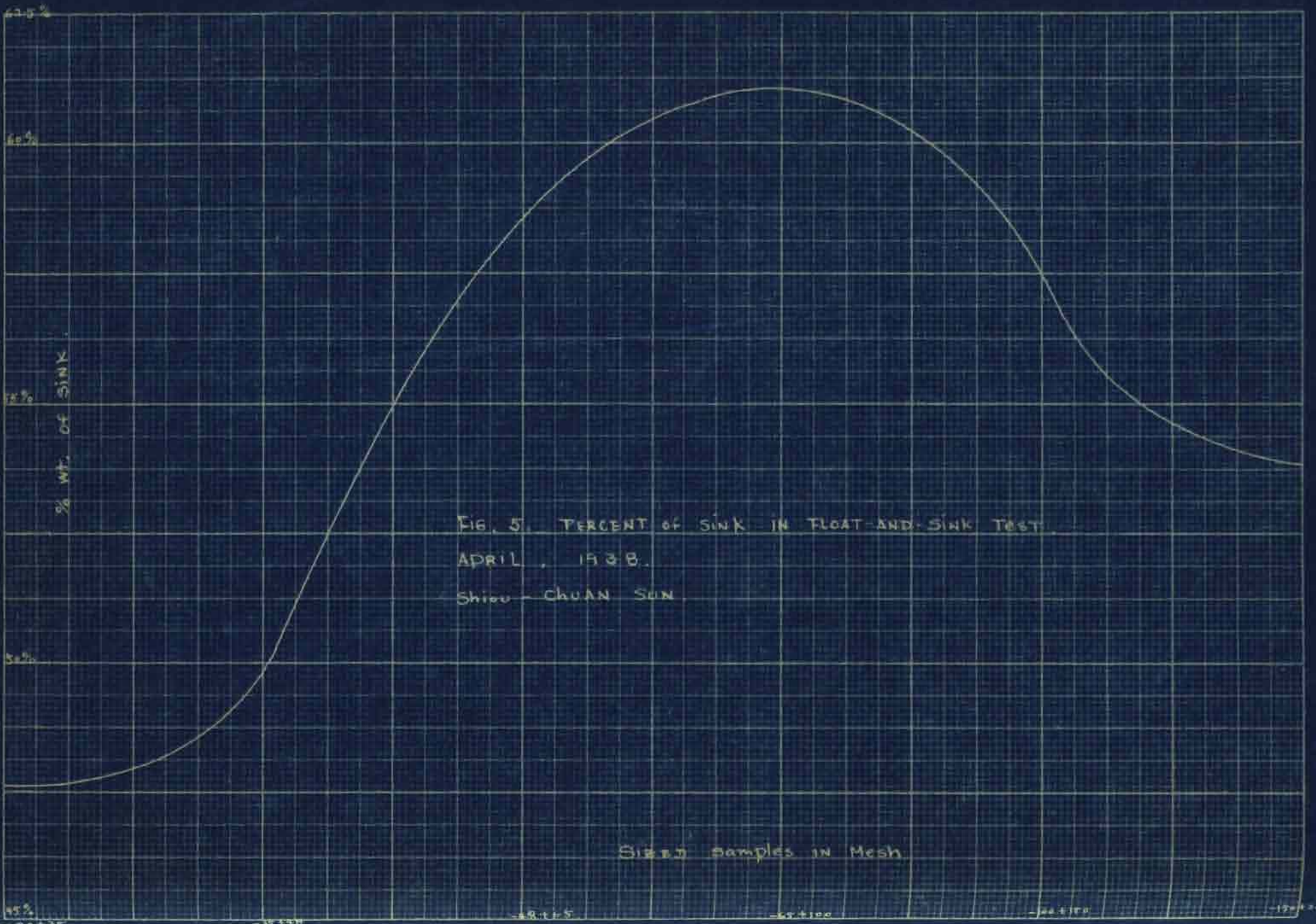
FIG. 5. PERCENT OF SINK IN FLOAT-AND-SINK TEST.
APRIL, 1938.
Shiou - Chuan Sun.

% wt. of sink

sized samples in mesh

The heavy liquid used in the present in-
vestigation was acetylene tetrabromide, having a[12]
specific gravity of 2.95. Accordingly, if there is
complete liberation between the component minerals,
at any particular size, the quartz, chert, and cal-
cite should report entirely in the float product,
and the fluorspar, barite and sulphide minerals in
the sink products.

A chemical or microscopic analysis should
then furnish the desired data concerning the size of
liberation.

Practically, the separation is not so clear-
ly defined, for:

(a) Complete liberation even in the finer size
    is never completely achieved.

(b) In finer sizes mechanical contamination and
    flocculation may occur.

Therefore, fluorspar may be found in both
float-and-sink samples. Sphalerite may occur in the
float sample occasionally even traces of galena may
be retained in the float samples.

---

[12] Sullivan, J.D., "Heavy Liquids for Mineralogical
Analysis" : Technical Paper No. 381, U.S. Bureau
of Mines, 1927, p.26.

Very useful information could have been obtained if float-and-sink tests had been made on the sink products in acetylene tetrabromide, using, say, methylene iodide, having a specific gravity of 3.3. This would have enabled a clear cut separation of the fluorspar, once the size of liberation had been reached. Unfortunately, methylene iodide is very expensive, and it was found impossible to use it.

Sized-ore aggregates from the screen analyses were used for float-and-sink tests. Separation was effected in a 300 cc separation funnel, acetylene tetrabromide being used as the heavy medium. The sink product was drawn off into a beaker and filtered through a filter paper. The float product was likewise filtered. The bulk of the heavy liquid which filtered through the paper could be recovered and used again. The float-and-sink products were washed in benzene, dried and weighed.

The results of the float-and-sink tests are given in Table VI.

(B) Microscopic Examination:

The microscope may be used to:

(a) Identify the minerals present in an ore.

(b) The relative abundance of the minerals.

(c) The interlocking occurring in the
    float-and-sink products.

(d) The grain size of the minerals.

From the viewpoint of the ore under investigation (b) and (c) were the most important points to be ascertained, especially (c), which should give the size of liberation and hence the size to which the ore would have to be crushed prior to concentration.

Preliminary microscopic examination showed that fluorite was liberated from quartz, chert and calcite at relatively coarse sizes. The major problem was therefore to ascertain at which size practically complete liberation of fluorite-sphalerite, fluorite-galena, and of galena-sphalerite occurred.

Sphalerite, to be accepted by a zinc smelter, must contain a very minimum of fluorite. Present day zinc smelters utilise the SO_2 obtained from the roasting of sphalerite concentrates for the production of sulphuric-acid by the contact

PROCESS. Traces of fluorine are ruinous to the catalyst used in the process.

There is no fixed maximum quantity of fluorite which may be permitted in galena concentrates, nevertheless it is desirable to keep the fluorite as low as possible if only for general metallurgical considerations.

Unlocking of galena from sphalerite prior to concentration is essential to the production of high grade zinc and lead concentrates.

The zinc content of fluorite concentrates should be reasonably low (less than 0.5%). Otherwise the zinc has a habit of causing trouble in the open-hearth slags.

From the above discussion it may be readily seen that the determination of the size of liberation of the ore under investigation is of paramount importance.

Results of the Microscopic Study

The float-and-sink products prepared from the screen analysis samples were chosen for examination. Float products were examined by the conventional petrographic methods. Sink products were examined by (1) petrographic methods and by

(20 briquetting, polishing, and using the metallographic microscope for the identification of opaque minerals.

The results of these investigations follow:

Minus 20 mesh plus 35 mesh sample

Sink in Sp. Gr. 2.95

This product consisted mainly of sphalerite and fluorite. Other minerals were galena, pyrite, barite, calcite and quartz. Considerable interlocking of sphalerite and fluorite occurred. Most of the galena was free, but the small amount of pyrite present was locked with the sphalerite. Barite was free, and present to a small extent. The quartz was wholly locked with the sphalerite and the fluorspar. Figs. (6), (8), (10), (12) show a typical section of the product.

Float in Sp. Gr. 2.95.

The minerals present in this product, in the order of their abundance, were calcite, chert, quartz, fluorspar and sphalerite. The first three minerals were essentially free but small quantities of quartz, fluorite and sphalerite occurred as locked grains.

Figs. (7), (9), (11), show a photomicrograph of a polished section of this product.

Minus 35 mesh plus 48 mesh sample

Sink in Sp. Gr. 2.95.

This product consists essentially of sphalerite, fluorite, and galena. Locking of sphalerite with fluorite and calcite is not as severe as in the corresponding coarser product. The galena is totally free. A typical section is illustrated in Fig. (8).

Float in Sp. Gr. 2.95.

This product is very much the same as the -20+35 mesh float product. Some sphalerite is present, locked with chert and calcite. Fig. (9) shows the appearance of this material under the microscope.

Minus 48 plus 65 mesh sample

Sink in Sp. Gr. 2.95.

This product consists essentially of sphalerite, fluorspar, and galena. Practically all of the sphalerite is free, a small amount being interlocked with fluorite. The galena is quite free. The fluorite contains only small quantities of interlocked sphalerite. Fig. (10) shows how free the sphalerite is from locked fluorite.

-35-

Float in Sp. Gr. 2.95.

This material consists of quartz, chert, and calcite. A little locked fluorite occurred and small amounts of sphalerite. See (Fig. 11).

Minus 65 plus 100 mesh sample

Sink in 2.95 Sp. Gr.

Galena and sphalerite are practically free of interlocked gangue minerals at this size. Like-wise the fluorite contains no contaminant sulphide minerals. Fig. (12) shows the almost complete freedom from interlocking.

Float in 2.95 Sp. Gr.

This product is quite clean and free from interlocked fluorite and sphalerite.

Sizes finer than 100 mesh

The float-and-sink products prepared from the -100+150 mesh and the -150+200 mesh sizes were examined by microscopic methods. Even less inter-locking between the various minerals occurred at these sizes than in the coarser sizes. However, finer size than 100 mesh would materially benefit the operation of separating the various minerals from each other.

Microscopic grain counts were made of each
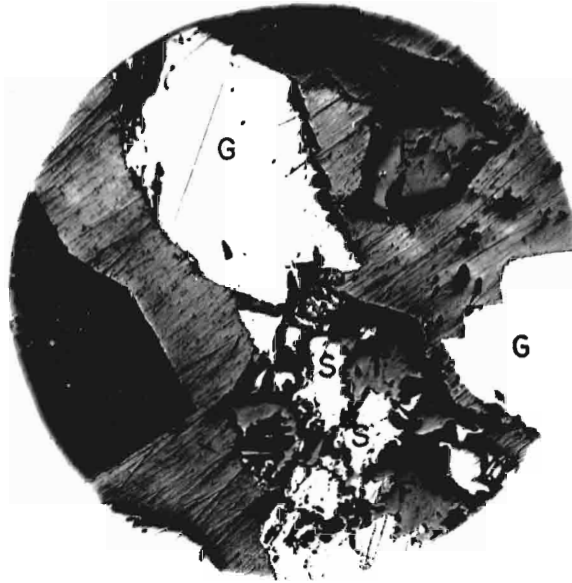
Fig. 6. Photomicrograph of a
Polished Section of the -20+35
Mesh sink product. X50. Show-
ing galena(G), fluorite(F),
calcite(C), sphalerite(S), and
Chert(Ch). The galena is coarse
and free from interlocking. The
sphalerite is badly locked with
the fluorite. The single particles
of chert and calcite are apparently
free.
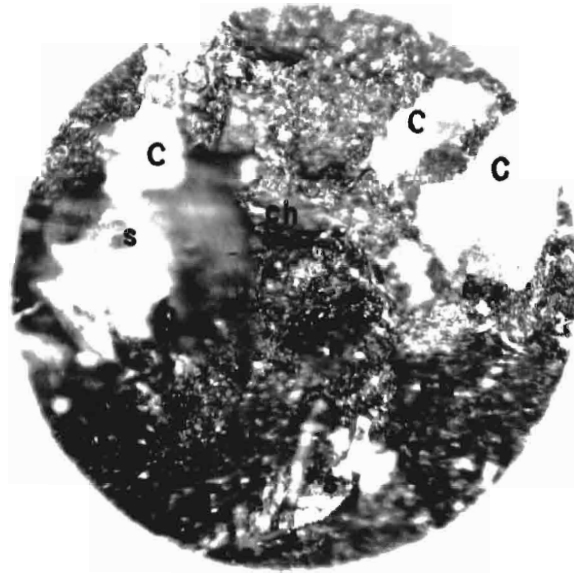
Fig.7. Photomicrograph of a Polished Section of the -20+35 mesh float product. X50. Most of the grains consist of chert (Ch) and calcite(C), sphalerite(S).

Fig. 8. Photomicrograph of a
Polished Section of the -35+48
mesh sink product. X30. Show-
ing galena(G), sphalerite(S),
and fluorite(F). Some inter-
locking between sphalerite and
fluorite is shown by the grain
in the upper left hand corner.
Very little calcite is present.
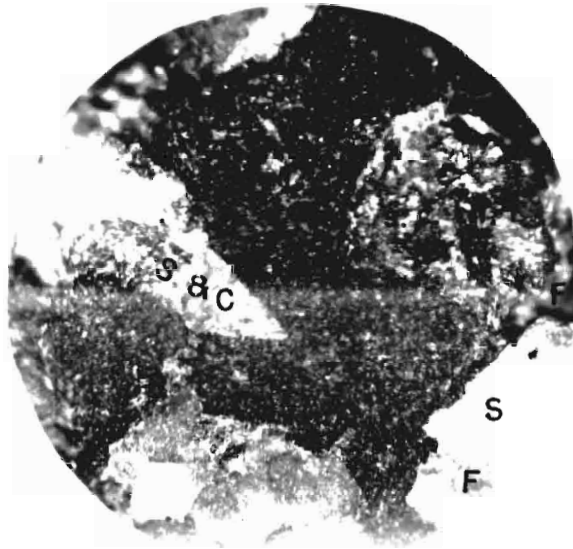
Fig. 2. Photomicrograph of a Polished section of the -35+48 mesh float product. X50. Showing sphalerite(S), Calcite(C), Chert (Ch), and Fluroite(F). The central grain shows rather bad interlocking between all four minerals.

Fig.10. Photomicrograph of a
Polished section of -48+65 mesh
sink product. X50. Galena(G),
sphalerite(S), and Fluorite(F).
The sphalerite is practically
free of locked fluorite and the
fluorite is locked with very
little sphalerite.
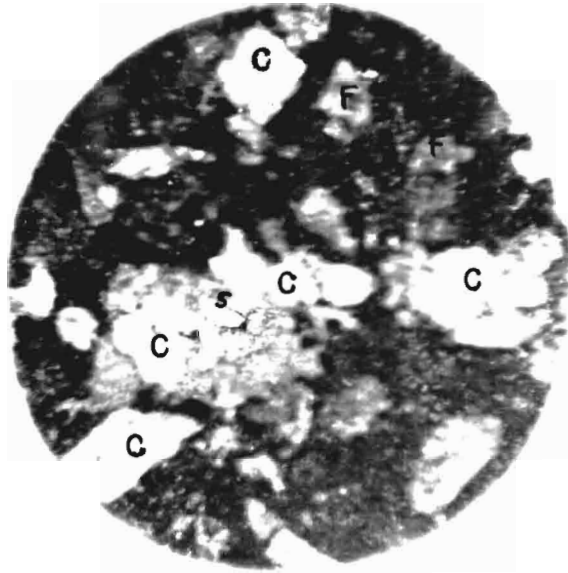
Fig. 11. Photomicrograph of a
polished section of -48+65 mesh
float product. X50. Chert, quartz,
calcite, sphalerite and fluorite.
The last two minerals are present
to only a small extent.

Fig. 12. Photomicrograph of a polished section of -65+100 mesh sink product. X50. Sphalerite(S) and fluorite(F). Virtually no interlocking occurs between these two minerals.
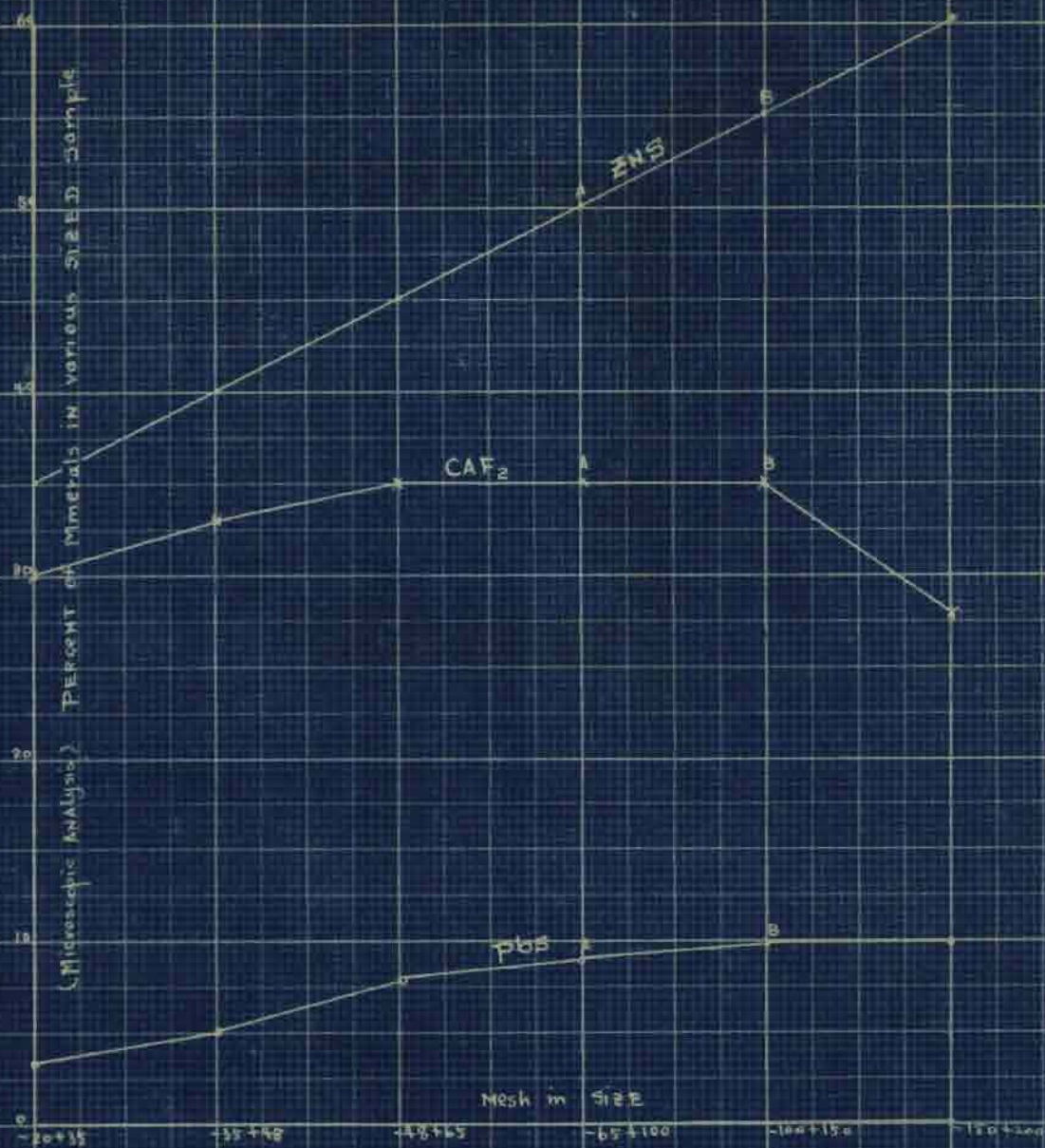
FIGURE. 12 a. SHOWING THE ELEMENTARY MINERALS OCCUPY THE PERCENTAGE OF VARIOUS SIZE of SAMPLES. (THE PART A.B. is the IDEAL SIZE HIGH RECOVERY AND HIGH LIBERATION. THIS FIG. CAN PROVE THE CONCLUSION A. B.)

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product. The results of the grain counts of the
sink products are given in Table (VII).

Table (VII) - Percent of Ores in Sink Samples.

Ore	-20+35 mesh sink	-35+48 mesh sink	-48+65 mesh sink	-65+100 mesh sink	-100+150 mesh sink	-150+200 mesh sink
Sphalerite	35%	40%	45%	50%	55%	60%
Galena	3%	5%	8%	9%	10%	10%
Fluorspar	30%	33%	35%	35%	35%	28%

Table VI - Percent of Ores in Sink Samples (microscopic
assay).

These results are plotted in Figure
The galena increases steadily in amount as the size
decreases. This may be attributed to the relative soft-
ness of the galena. It is not clear why the percentage
of fluorite should suddenly decrease in the -150+200
mesh size.

(D) Conclusions

(A) The microscopic study of the sulphide-
fluorspar ore very definitely furnishes the answer to
the question "to what size should the ore be crushed
in order to physically liberate the galena from various
gangue minerals and from sphalerite, the sphalerite
from the fluorite and associated gangue minerals, and
the fluorite from small amounts of sphalerite."

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It is evident from the results of the investigation that galena is a free mineral at a relatively coarse size, about 35 mesh. The association of sphalerite with fluorite is so intimate, however, that a considerably finer grinding is necessary to be certain that a sphalerite concentrate low in fluorite and a fluorite concentrate low in sphalerite could be obtained by ore dressing methods. The upper limit in this case is approximately 100 mesh. In other words, the ore, either prior to or following separation of the galena, would have to be ground to 100 mesh in order that the zinc and fluorite concentrates could meet market demands for purity.

(B) It is evident that gravity concentration would not be satisfactory as a method of preparing lead, zinc, and fluorite concentrates from this ore. Conceivably the lead could be separated at approximately 35 mesh by table concentration but the remainder of the ore would have to be crushed to 100 mesh to effect separation of the sphalerite and fluorspar. This is not feasible by gravity methods, on account of (a) the fine size and (b) the small difference in specific gravity between the fluorite and the sphalerite.

CHAPTER THREE

Flotation Concentration

(I) Definition of Flotation:

Flotation is a method of wet concentration of ores in which separation of mineral from gangue is effected by causing the mineral to float at or above the surface of a body of liquid pulp while the gangue remains submerged. This particular method of concentration utilises the surface properties of minerals and has nothing to do with the specific gravities of the minerals to be treated _except when the minerals are too coarse_. The method operates, in general, only on particles smaller than 0.5 mm. diameter. Minerals that float readily are those of metallic, resinous or adamantine luster, such as the base - metal sulphides; those that are not readily floated are the vitreous or earthy gangue minerals. This is a generalisation and not always true. Thus galena can be separated from blende; fluorite, calcite, and apatite may be separated from quartz and almost all other silicates; coal can be separated from slate, and mica from other silicates.

(II) **Evolution of Flotation:**

      (A) **Film Flotation(skin flotation)** [13]

            1860-1885.

By the difference of the "Resistance to wetting" of the surfaces of metallic minerals compared with that of gangue minerals, the metallic ores can be floated on the surface of water, but the gangue minerals will be easily wetted and will sink. If a sulfide ore is crushed, dried and sized through, say 0.3 or 0.2 mm, and brought gently onto the surface of a body of still water a certain number of the particles will float. The floating particles will contain a higher proportion of sulphide minerals than was present in the original ore. But the gangue minerals will not float.

Fig. (13) shows the principle of film-flotation. Metallic ore may be floated due to its high contact angle with water, so the resulted force T' being greater than the weight W of the mineral.

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13   Hoover, Theodore J.; "Concentration Ores by Flotation" - The Mining Magazine, Salisbury House, London, E.C., 1914, pp.1-5, 69.

But gangue minerals possess a low contact angle with water, so the floating force T'' is smaller than the particle weight W, and the gangue particles are forced to sink. In Fig. (13) is shown the common type of film flotation machine. It consists of two tanks (A) and (B) filled with water. A roller (C) with corrugated rubber belting, rotates in the direction indicated. The roller carries a thin layer of water. Dry ore is fed onto the surface of the revolving roller by means of the shaking feeder (E). Gangue minerals tend to wet and sink into the grooves, while the minerals of metallic luster tend to float. When the floating and submerged minerals are carried over to the point where the surface of the liquid in the tank intersects the surface of the roller, the floating mineral rides out onto the water surface because the surface film is continuous over the tank and roller. A gentle current is maintained from pulley (D) toward the small roller (F) by reason of constant addition to the surface film at (C) and constant removal at (F) by the traveling belt (G). The less tightly held material in the film is shaken out and settles to the bottom of tank (B). This is the middling product. The floating concen-

AIR

a

H₂O

METALLIC ORE

(a)

AIR

b CONTACT ANGLE.

H₂O

GANGUE (EARTHY LUSTER)

(b)

(a) AND (b) Show the contact angle of H₂O with metallic ore is greater than that of water with gangue minerals. Namely, metallic ore posses higher "resistance to wetting".

T'   T'   T'   T

a   a

H₂O   GANGUE   H₂O

H₂O   METALLIC ORE   H₂O

W

(c.)

W

(D)
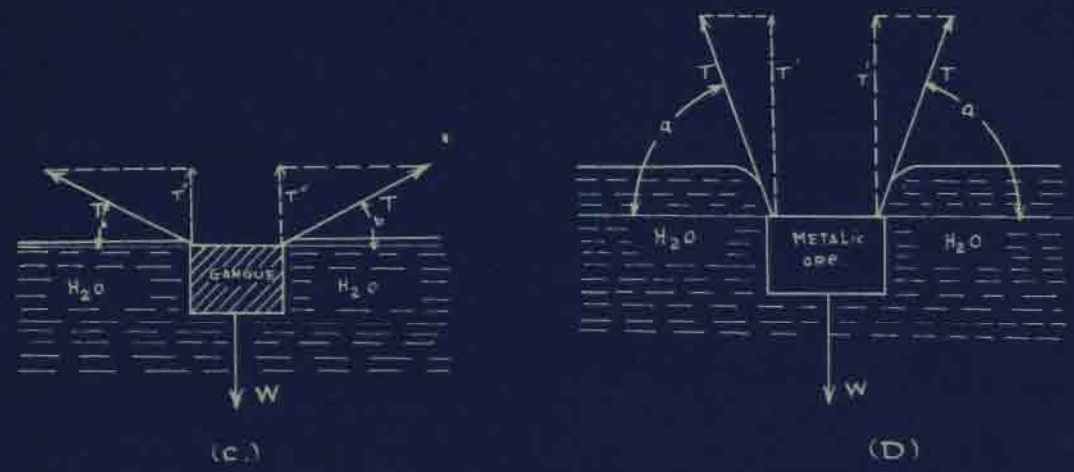
(c) & (D) Show high contact angle making high flotability. C & D are same size, shape, and wt. but T' is larger than T".

E

C   G   D   CONCENTRATE

F

MIDDLING (CONCENTRATE)

H₂O

H₂O

B

TAILING   A

A. & B TANKS

C. Roller.

D. Pulley.

E. Shaker feeder.

F. Roller

G. Belt.

(e) Wood Dry-Feed Film-Flotation machine.

FIG. 13. Principle and machine of Film-Flotation.

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trate overflows the lip of the tank (B). Details of
this process are given by Hoover[14]. However, this
process is no longer used.

(B) Oil Flotation - 1872-1914.

"Bulk oil flotation" and "oil-buoyancy flo-
tation" are other names for the same method. The
process depends upon the interfacial forces at the
contact of a mass of oil and water for selecting and
holding sulfide minerals, and upon the buoyancy of
the oil in water for the levitation of selected
sulfide.

Operation of the process consists in mixing
relatively large quantities of oil with finely
ground ore, either before or after admixture with
water, then allowing the mixture of ore, oil, and
water to stratify. If the oil is of lower specific
gravity than water (or the pulp), a load of solid,
predominately metallic mineral, is carried at the
interface between the oil and water. By overflow-
ing the oil layer with a thin layer of underlying
water, this mineral load can be separated from the

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14 (a) Taggart, A.F.; - "Hand Book of Ore Dressing"
        New York, John Wiley and Sons, Inc., 1927,
        pp. 780-783.
    (b) Hoover, Theodore J.; "Concentration Ores by
        Flotation" - The Mining Magazine, Salisbury
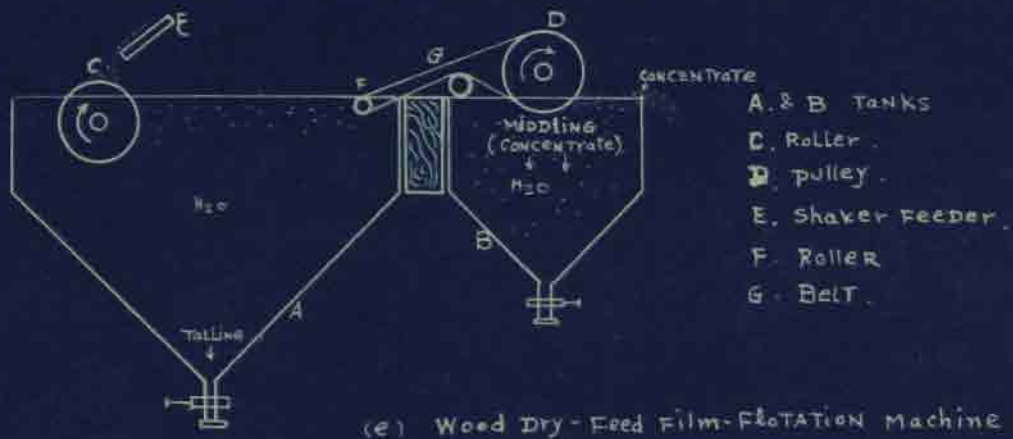   House, London, E.C., 1914, pp.1-7, pp.69-72.
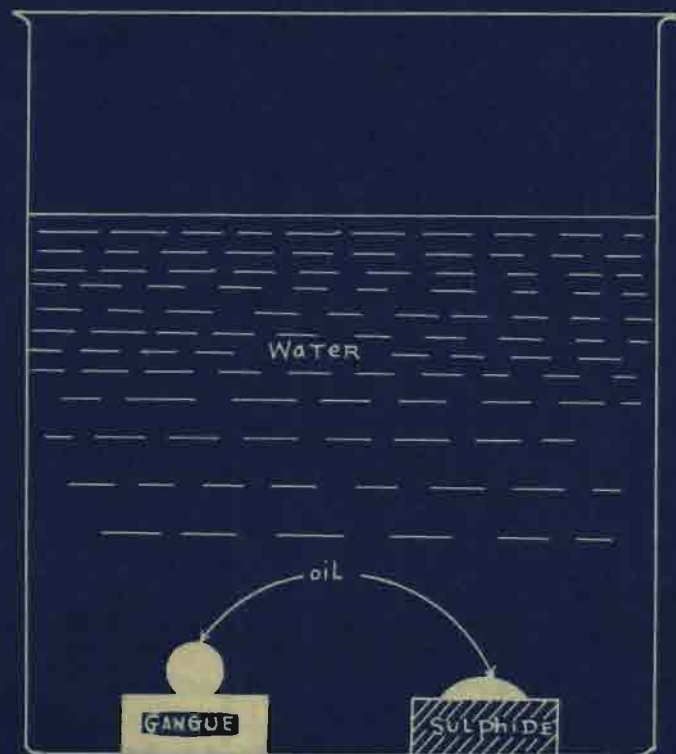
FIGURE 14.   BEHAVIOR OF OIL AND
WATER AT GANGUE AND MINERAL
SURFACE. (PRINCIPLE OF OIL FLOTATION)

settled gangue. The theory of oil-flotation is illustrated in Fig. (14). This process was replaced by froth flotation.

(C) Froth Flotation - 1901-1905 [15]

Froth flotation comprises two entirely different types of processes which resemble each other only in the fact that in both the concentrate in the form of a froth or foam composed of gas, liquid, and solid water. In the early days the mineral that was floated was mineral of metallic luster, but greater knowledge of reagents and controlling conditions have now made it possible to float other kinds of mineral.

The processes differ fundamentally both in the place in which concentration is doen, and in the mechanism of the selection of sulfide ore from gangue. On the basis of the first difference the process may be classified as pulp body process and bubble-column process. On the basis of mechanism of the selection of sulfide ore from gangue, the contact angle (see Fig. 18), and the behvaior of oil on

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15 Hoover, Theodore J.; "Concentration Ores by Flotation" - The Mining Magazine, Salisbury House, London, E.C., 1914, pp.120-134.

solids (see Fig.19), has already been presented. The metallic particles after oiling are easily wetted by the gas bubbles and carried to the surface of the pulp. Gangue minerals are oiled with difficulty but are easily wetted by water and then sink down to the bottom.

(D) Differential and Selective Flotation. 1906 to date. [16]

"Differential flotation" is used in contradistinction to the phrase "bulk flotation". The latter indicates an operation in which all of the minerals of the general class, e.g., sulphides, are separated by flotation from all minerals of the non-sulphide class; the first term describes a separation effected between two or more minerals of the same class, e.g., lead sulphide from zinc sulphide, or one non-metallic mineral from another. Typical cases are: Galena from blende, pyrite from blende, chalcopyrite from pyrite or pyrrhotite, chlacopyrite from blende, mica from rock-forming silicates, cassiterite from quartz, etc.

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16 (a) Hoover, Theodore J.; "Concentration Ores by Flotation" - The Mining Magazine, Salisbury House, London, E.C., 1914, pp.135-164.

(b) Taggart, A.F. - "Hand Book of Ore Dressing" - John Wiley & Sons, New York, 1927, pp.790-828.

Differential flotation is performed by careful control of the following factors: Intensity of frothing, frothing agents, condition agents, aeration, agitation, concentration of hydrogen-ion, size of particles, pulp density, etc., which will be briefly described hereafter.

The invention of collecting reagents in 1922, and the introduction of xanthates in 1924, made differential flotation relatively easy. In this paper, "flotation" is equivalent to "differential flotation".

(E) Classification of Differential Flotation Tests.

According to the U.S. Bureau of Mines[17] flotation testing is considered under three heads, as follows: (1) open-circuit batch tests, (2) closed-circuit batch tests, and (3) closed-circuit continuous tests.

(a) Open-circuit batch flotation tests: A sample of suitably ground ore; usually 125 to 2000 grams, is treated in a laboratory flotation cell

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17   Dietrich, W.F.; Engel, A.L.; Guggenheim, Morris; "Ore Dressing Tests and Their Significance". Information Circular, U.S. Bureau of Mines - No. 3328, pp. 24-25.

without circulation of the intermediate products. Such tests, serve the purpose of determining the kind of flotation and conditioning reagents that are best suited to the ore being treated, the degree of grinding necessary, and the probable recovery and grade of concentrates. They do not determine the quantity of reagents required, or the ultimate disposal of the intermediate products.

(b) Closed-circuit batch tests: These tests involve the same equipment and methods used in the open-circuit batch tests, but a series of tests is made to permit the return of intermediate products and flotation water for re-treatment with the feed of a successive test.

(c) Closed-circuit-continuous tests: The tests are conducted with a ball mill and classifier in closed circuit, followed by a bank of flotation cells. The entire flow sheet is arranged to give a continuous flow of pulp. In the laboratory, these tests are similar to pilot-mill tests.

(d) Factors influencing the choice of flotation testing methods: Open-circuit batch tests serve the purpose of determining the amenabil-

ity of the ore to flotation and yield approximate data as to the grade of concentration, percentage recovery, kind and quantity of reagents, and required degree of grinding. The chief weakness of these tests is that intermediate products are not retreated.

Closed circuit tests are necessary, when the open-batch tests indicate that an excessively large proportion of the valuable minerals enters intermediate products, which in turn must be treated.

The continuous closed-circuit test on the customary scale of 100 to 150 pounds of ore per hour consumes so much time and labor that it should be used only as a last resort to solve the real difficulties which can not be solved by the less elaborate tests and which should be solved before the erection of a pilot-mill at the property is justifiable.

(III) - Size of Particles in Flotation.

(a) Effect of Particle Size on Flotation :-
Satisfactory separation of an ore into concentrates an tailings is possible only when the individual minerals in the ore are physically separated. Sizing tests and microscopic studies show that liberation is more nearly perfect in the finer sizes.

Examination of the coarsest portion of an ore pulp affords a critically adverse picture of liberation.[18]

It is not practical to carry liberation to completion; indeed, it is economically desirable to strike some happy medium between complete liberation and one that is metallurgically ineffective.

By the experiments of Gaudin[19], we know the coarse non-polar particles may well show reduced flotability. To a certain extent, the flotability of the non-polar particles may be increased by the decrease of size.

Broadly speaking the following conclusions have been reached by the experiments at the Montana School of Mines[20].

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18   Gaudin, A.M.; "Flotation" - McGraw-Hill Book Co., New York, 1932, Tables 16,18,19,21. pp.140-146.

19   ibid, p.152

20   Gaudin, A.M., Grott, John O., and Henderson, H.B., "Effect of Particle Size on Flotation". Technical Publication No. 414, American Institute of Mining and Metallurgical Engineers, p. 23.

(1) The usual notion about the relative ease of flotation of very fine particles does not agree with the facts.

(2) There is a time sequence of flotation with regard to particle size, the medium coarse particles floating first.

(3) No successful method of floating extremely fine pulps has been found.

(4) Recovery is at an optimum in a certain well defined size range.

(5) Selection is at a optimum in another well defined size range.

(b) Dry Versus Wet Grinding: Dry grinding of ore prior to flotation is generally unsatisfactory and is not representative of plant practice. Flotation tests on dry-ground samples often give recoveries 10 to 20 percent lower than when the samples are wet-ground. This is due to increased oxidation during dry-grinding.

(c) Flint Versus Steel Balls: In plants, grinding of most flotation feed is done in steel mills with steel or cast iron balls. But in laboratory work porcelain mills with flint pebbles are preferred, because the iron contamination in

Size . Mesh .

FIG . 15 .   RELATIONSHIP BTWEEN PARTICLE
SIZE AND COMMERICAL AVERAGE OF LOSSES
AT ALL PLANTS STUDIED .

21 : After Technical publication No. 414 . A.I.M.E.

laboratory grinding with steel balls is exaggerated compared to plant practice. This is primarily due to the relatively higher ratio of exposed grinding surface per unit of ore ground. Another reason is that the intermittent use of the laboratory mill favors excessive rusting. The advantage of the pebble mill is that it gives a constant conditioning factor. The effect of plant grinding with steel balls may be neutralised by the addition of an alkali to the grinding circuit.

(IV) - Pulp Dilution and Pulp Consistency.

For general purposes the suitable pulp density is 25% of solids, namely, the ratio of ore to water is 1:3. It is desirable to keep low dilution for the following reasons:

(a) Saving in water.

(b) Less cost of handling.

(c) Less cost of treatment, because of the smaller amount of reagents required.

(d) Increased capacity of flotation machine.

On the other hand, decreased dilution increases the mechanically entrained load of solids in the froth, so that the froth will be dirty. This is illustrated by the following table.

-60-

Table (VIII) - <u>Effect of Pulp Dilution on Flotation</u>

<u>Results.</u>

[22]

Charge in Cell at Start of Test gms.		Pulp Consistency	Concentrate Load %	Tailing Load %	Actual Load Lost in Tailing.
2400	2800	3.5	43.4	0.12	2.2
1800	3000	3	56.6	0.14	1.9
1200	3200	8	59.0	0.14	1.4
900	3300	11	62.4	0.14	1.1
600	3300	17	63.9	0.27	1.4
450	3450	23	68.2	0.45	1.8
300	3500	35	74.8	0.56	1.5

From Table (VIII) it may be concluded that the recovery decreases but the gangue rejection increases as the pulp is made thinner. In practical work the pulp dilution should be less for roughing operations but greater for cleaning operations.

Dilution is the ratio of the weight of liquid to that of solids in an ore pulp. Pulp consistency is the ratio of volume of liquid to the volume of solids in an ore pulp. Pulp consistency is

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22   Gaudin, A.M.; "Flotation" - McGraw-Hill Book Co., New York City, 1932, p.118.

always larger than pulp dilution and it is physically more significant altho less frequently used. Pulp consistency ranges 13:1 to 4:1.

(V) - **Effect of pH on flotation**.

The flotation of certain minerals may be helped or may be hindered by pH regulation. The following examples show this :

(1) In the flotation of pyrite, the effect of pH is very marked, as can be seen readily by Figure 16.

(2) In lead and zinc ores, a satisfactory recovery of sphalerite may be obtained only by control of the pH within narrow limits; if the pH is over 10.4 galena will be depressed.

(VI) - **Reagents**.

The reagents which have been used in and have been proposed for flotation number more than three thousand. In this paper only those common reagents which are used in testing work will be mentioned [23].

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[23] For a more extended discussion of flotation reagents, see the following: American Cyanide Co.; "Flotation Reagents." - 30 Rockefeller Plaza, New York, Author; January 1937, p. 19. Weinig,A.J., and Palmer, I.A., "The Trend of Flotation", Bull., Colorado School of Mines, Vol.24, No.4, Oct.1929, pp.21-25. Taggart, A.F., Taylor, T.C., and Ince, C.R. - "Experiments with Flotation Reagents". Tr., Vol.87, AIMME, Milling Methods, 1930, pp.285-368.
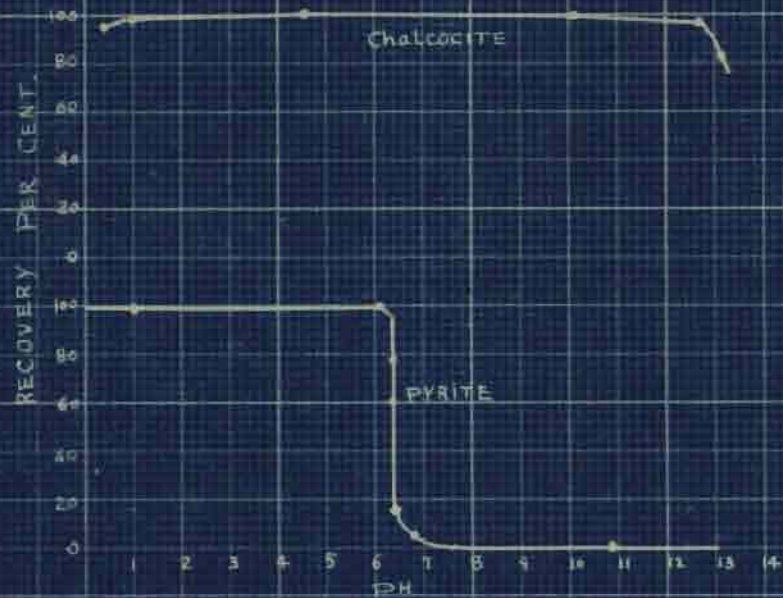
FIGURE 16

RELATION of RECOVERY To HYDROGEN—ION CONCENTRATION

(AFTER GAUDIN, COPPER ORE FLOTATION)

Reagents are generally classified as follows: (a) frothing reagents, (b) collecting agents or so called promoters, (c) depressing agents, (d) activating agents, (e) deactivating agents, (f) cleansing agents, (g) pH regulators, (h) protective colloids, (j) antitoxic agents, and (k) dispersing agents.

(A) _Frothing Agents_ - As a stable froth cannot be formed in pure water, a frother is required in flotation. When, say, phenol (about 0.5 lb. per ton) is used the bubbles of gas dispersed in the pulp are smaller, more elastic, and reach the surface without bursting, forming a more or less coherent froth.

From Gibbs' absorption equation[24] we know that salt solutions have higher surface tensions than water, whereas aqueous solutions of alcohol have a lower surface tension than water. There is therefore an excess of alcohol in the surface layer, i.e., the alcohol is _adsorbed_. Another conclusion to be derived from Gibbs' equation is that large amounts of substances which raise the surface tension of a liquid have to be added to it to produce a material

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24   Extended Discussion of this equation, see: Gaudin, A.M.; "Flotation" - McGraw Hill Book Company, Inc., New York City, pp.17&18.

change in surface tension, but that small amounts of
a substance lowering the surface tension may be
sufficient to bring about a drop in surface tension
equivalent to the rise obtained otherwise . This is[25]
the reason that all frothing agents used in practice
are substances that lower the surface tension of
water. They are extremely effective in lowering the
tension sufficiently, even if used in very small
amounts.

The frothers are organic compounds, the
longer the "CH_2" chain the less the solubility and
the greater the capacity to lower the tension of
the water. (see Table IX).

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[25] Willows, R.S.; and Hatschek, Emil; "Surface
Tension and Surface Energy and Their Influence
on Chemical Phenomena." - Churchill, J.A.;
London, 1915.
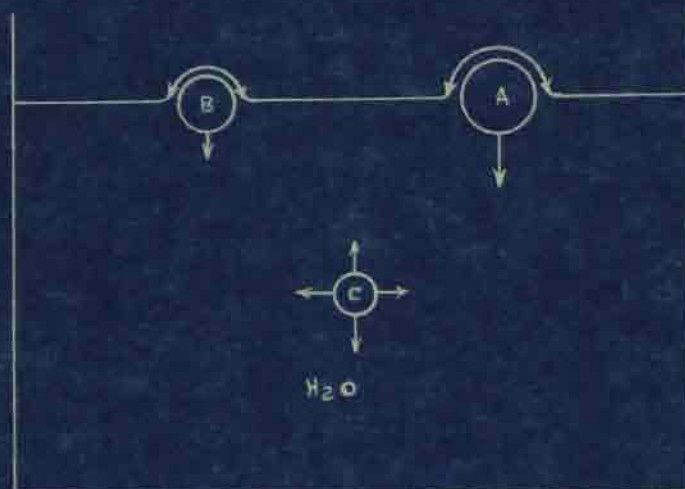
FIG. 17. SURFACE TENSION FORCES THE bubbles go DOWNWARD

A. Bigger bubble subject more Force of surface-Tension
B. Smaller bubble subject less Force of Surface-Tension
C. Bubble not reach surface yet, Subject No Surface Tension.

$$H_2O \longrightarrow H^+ + OH^-$$
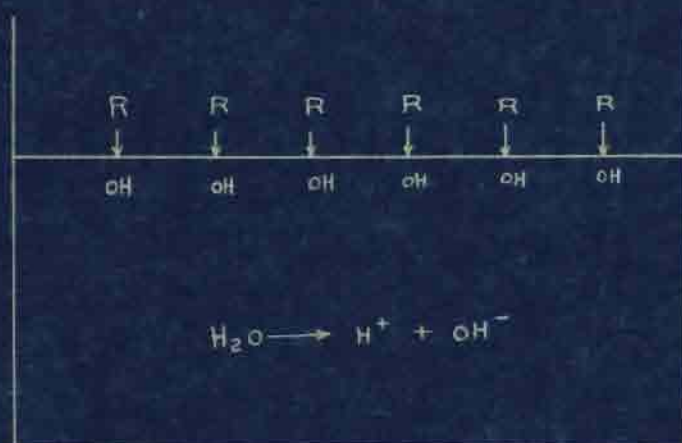
FIG. 18. Carbon Atom of Frother DECREASE Surface-Tension.

R = carbon atom, of Frother.
OH = polar part of Frother.

Table (IX) - Relationship Between Length of Hydro-
Carbon Chain of Organic Compounds and
Lowering of the Surface Tension of
Water Caused by Their Addition.

Substance	Number of Carbon Atoms	Approximate Amount (part per million) Needed to Depress the Surface Tension of Water 5 dynes at 20 ± 2°C.
Acetic acid	2	15,000
Propionic acid	3	4,000
Iso-butyric acid	4	2,000
Iso-valeric acid	5	850
Iso-capraic acid	6	280
Heptylic acid	7	70
Caprylic acid	8	20

Frothers Used in Practice
[26]
 a. Pine oil: This material has marked
collecting properties for graphite, coal, molyb-
denite, sulfur and talc, but no collecting value
for metallic minerals.

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26 American Cyanide Company: "Flotation Reagents",
30 Rockefeller Plaza, New York City, p.11.

b. Cresylic acid: Possess distinct collect-
ing properties for lead and copper sulfides.

c. Frother 60: Widely used in the flota-
tion of non-metallics.

d. Barrett. No. 4, No. 410, and No. 634:
These are coal tar creosote oils.

e. Crude petroleum: Limited use in flota-
tion of sulfidized lead ores.

(B) Collecting Agents

Oil collectors and chemical collectors:
The term collecting agents goes back to the days of
flotation with oils, at which time it was used to
designate certain oils, which were capable of bring-
ing sulfide minerals to froth in great abundance.

Chemical collectors are collecting agents
which exert their action by adhering to the surface
of certain mineral particles, either in their
natural state or in some altered chemical form,
forming there a non-polar coating that repels water
but attaches itself readily to gas bubbles or to
non-polar media (oil droplets). Different agents
have different re-activities with different
minerals. This is important in selective flotation.

(a) <u>Principles of Reaction of Collectors</u>

(1) The theory of less solubility:-

Xanthates are made by carbon disulfide, alka-
linity solution, and alcohols. The chemical formula
of xanthate can be expressed as:

$$KOH + CS_2 + CH_3\,CH_2\,OH \quad CH_3\,CH_2O - C \underset{S-K}{\overset{S}{<}} + H_2O$$

$$H - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - O - C \underset{S-K}{\overset{S}{<}} + H_2O \quad \text{(Ethyl Xanthate)}$$
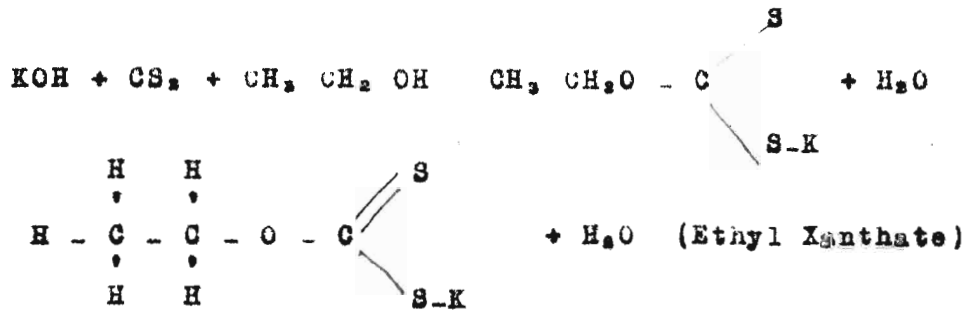
The base part of xanthate will be soluble in
water, and the organic part will react with sulfide
minerals as galena or sphalerite.

$$PbS + 2KEX = \underset{\text{(less soluble)}}{Pb\,(EX)_2} + K_2S$$
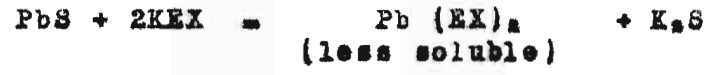
After xanthate was added with galena, a
chemical reaction took place at the surface of
galena. A non-active film coated the surface of

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28 Extension Discussion, see:
(a) Taggart, A.F., Taylor, T.C., Ince, C.R., Trans.,
Vol. 87, AIMME - Milling Methods, 1930, p.285.
(b) Wark, I.W., and Cox, A.B., - "Principle of
Flotation" - Transaction, Vol. 112, American Insti-
tute of Mining and Metallurgical Engineers, Milling
Methods, 1934, p.189.

galena. The coated film is non-polar and difficult to be soluble, and it is easily wetted by air but diffi-cult to be wetted by water. The coating of galena by less soluble film is illustrated by Figure (18a).

(2) Abstraction Theory:- Galena is allegedly easily oxidized in the mine or during grinding, and the coating of lead sulphate is supposed to abstract xan-thate ion from solution and produce equivalent sul-phate ion.

$$PbS + 2O_2 \longrightarrow PbSO_4$$

$$PbSO_4 + 2KEX \longrightarrow Pb(EX)_2 + \boxed{SO_4}$$

(3) Absorption Theory: As different minerals possess different powers of absoprtion for the xan-thate or other collecting reagents; therefore the degree of coating of non-polar part of collectors upon the surface of minerals are also different. The flotatbility of the minerals are different too. These can be explained by the Schuman Series: (See Table X).

$$(PbS + 2KEX \longrightarrow Pb(EX)_2 + K_2S)$$
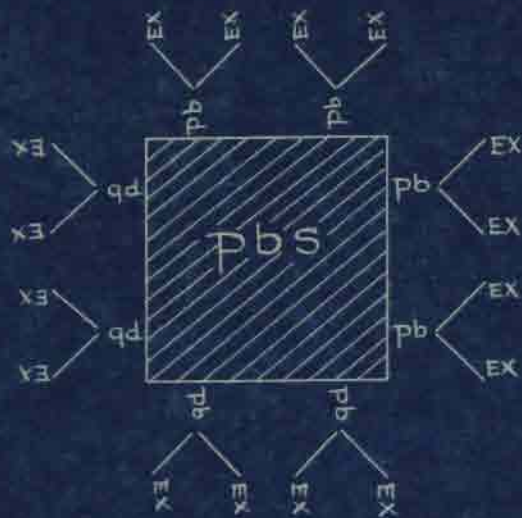
FIGURE 18a. LESS soluble xanthate film covers
the easily soluble galena to make it float
better.
1938. S. C. Sun.
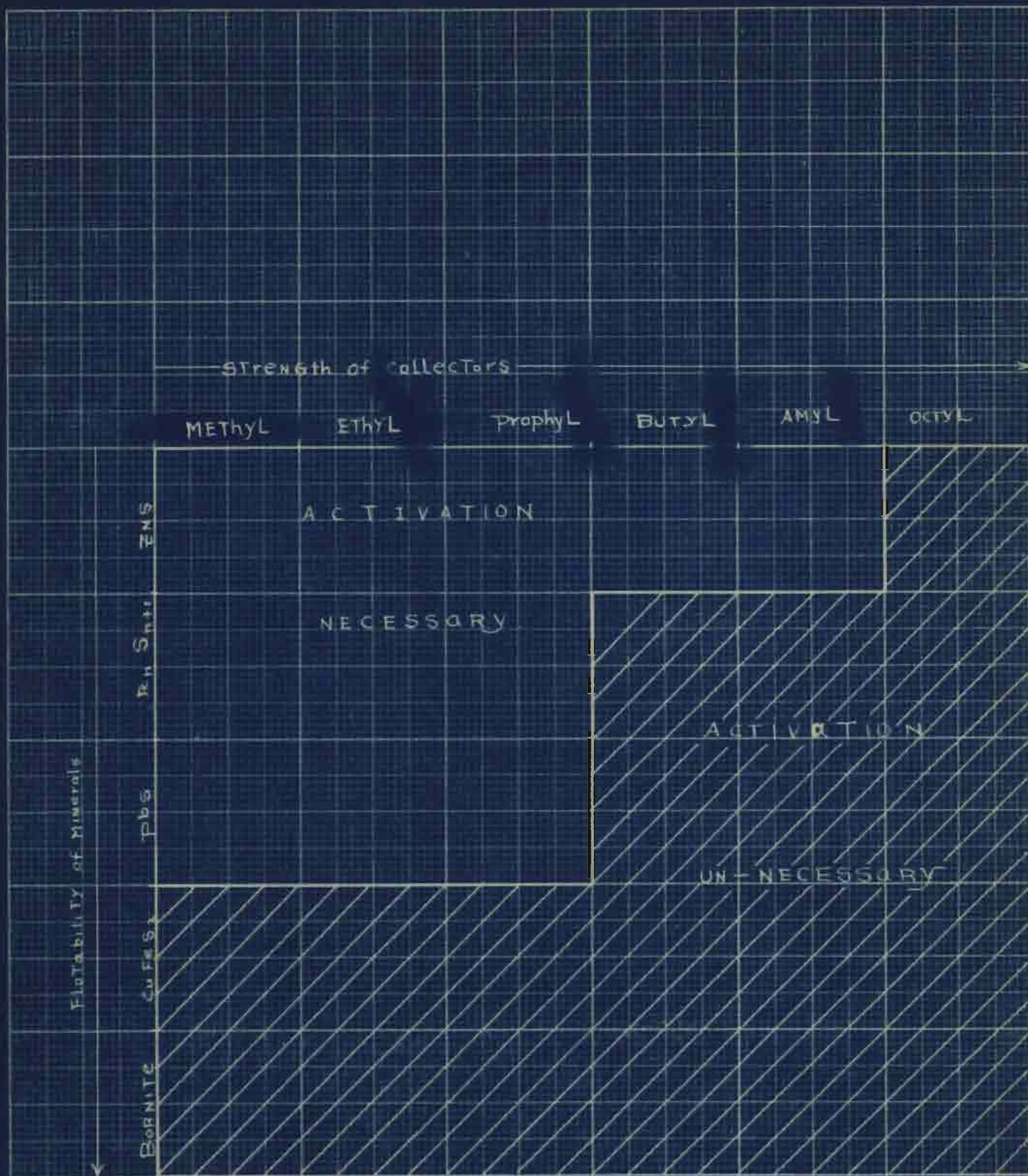
Fig. 19. Strength of Collector are Proportional to Length of Hydrocarbon-Chain

Flotability are Effected by Strength of Collector

Table (X)   The Schurman Series.

Minerals	Solubility of Sulphide in H_2O	Solubility of Xanthate	Flotability
Fe sulphide			
Zn sulphide			
Pb sulphide			
Cu sulphide			
Ag sulphide			
Hg sulphide			

(4) Hydrocarbon-chain Theory:- The longer the hydrocarbon-chain of the collector, the heavier the coating it will place upon the surface of minerals and the higher the recovery. See Fig. (19).

Ethyl Xanthate   - CH_3CH_2

Propyl Xanthate   - $CH_3CH_2CH_2$

Butyl Xanthate   - $CH_3(CH_2)_3$

Amyl Xanthate   - $CH_3(CH_2)_4$, etc.

Collectors used in practice:[29]

(a) Xanthates.

(b) Aerofloats.

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[29] Detail see: Gaudin, A.M.; "Flotation" - McGraw-Hill Book Company, Inc., New York City, 1932, pp. 68-78

(c) Thiocarbonates.

(d) Alpha Naphthylamine.

(e) Collecting oils :- Coal tar creosotes,
wood tar, crude oil in high sulfur.

(f) Fatty acid and soaps.[30]

a. Oleic acid.

b. Palmetic acid.

c. Heptylic acid, pelargonic acid, etc.

(C) <u>Conditioning Agents</u>.

If an ore settles rapidly and cleanly it may
be due entirely to freedom from colloids, or to acidity.
If colloids are present, they may be detected micro-
scopically. Soluble salts are detectable by colora-
tion of the ore or grinding water. The acidity or
alkalinity of the soluble salt can be measured by
pH determination.

When soluble salts are evident, soda ash
is used in quantities ranging from 0.5 pound to
2.0 pounds per ton of ore; in order to obtain the
proper pulp alkalinity, soda ash in excess tends to

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[30] Extended Discussion see: Coghill, Will H., and
Clemmer, J.Bruce; "Soap Flotation of the Non-
Sulfides" - Technical Publication No. 445,
A.I.M.M.E., 1932, p.16.

increase frothing with some ores, which results in less recovery of the desired mineral, the froth becomes watery. Sometimes the excess soda ash will increase the flotability of gangue minerals. When calcium salts are present in the pulp a combination of lime and soda ash may be necessary to precipitate them. Since lime strongly affects flotation, it must be used with care.

When colloids are present, and it is necessary to deflocculate or disperse them, sodium silicate is used. The amount of silicate added ranges upwards of a fraction of a pound per ton of ore. It will give high grade concentrates free from slime coating, but if present in excessive amounts, it will cause a weaker, more brittle froth, and hence a lower recovery. Acid circuits, are not used in modern flotation, but sulfuric acid may be used in conjunction with some other conditioning reagents to get best results and are sometimes used to flocculate the pulp. Caustic soda (NaOH) tends to increase frothing and to decrease the grade of concentrates and recovery. In non-sulfide flotation it may be used with sodium oleate to promote the efficiency of oleic acid as a collector.

Lime is widely used as a depressant, particularly in sulphide flotation, where separate concentrates of several sulphides are made, or where one sulphide is depressed while another is floated. Sodium cyanide is used as a depressant for sphalerite and other sulphide minerals. Zinc sulphate does not give very satisfactory results when used alone as a depressant for sphalerite. It is often used in conjunction with sodium cyanide to depress blende. Potassium dichromate is a depressant for galena but is not often used. Lactic acid is a depressant for mica and some other silicates. Sodium sulphite, hyposulphite, hypochlorite and other depressants have been used on individual ores with successful results. Copper sulphate is widely used as a general activator. Sodium sulphide is an activator for metallic carbonates and oxidized sulphides. An excess causes the formation of poor froths, and in certain concentrations, tends to flocculate the entire pulp. At other concentrations it is a dispersing medium. In flotation of non-sulphide minerals various metallic nitrates have sometimes been used as activators.

(VII) - Flotation Concentration Tests on Sulphide Fluorspar Ore.

It has already been pointed out that for the preparation of zinc and fluorite concentrates the ore must be ground to 100 mesh. Ten pounds of the broken ore were taken and crushed by a laboratory jaw-crusher through approximately 4 mesh. This material was then crushed through a laboratory roll-crusher to 48 mesh, the rolls being in closed circuit with a 48 mesh shaking screen. This method of crushing reduced the production of unnecessarily fine material. Batch flotation tests required 200 to 250 gms. of ore ground through 100 mesh. Hence batches of ore of this size were stage ground to size in Abbe' pebble mills, using flint pebbles and distilled water as the liquid medium. The -100 mesh ore was then filtered and flotation tests commenced.

Laboratory flotation cells of the minerals separation type were used for the flotation tests. They were of 250 gm. capacity.

Preliminary flotation tests were made, using empirical reagent charges based on quantities used on ores of similar mineralogical constitution. For example, in the initial test 0.4 lb. of soda ash (Na_2CO_3) was used per ton of ore. This condi-

tioned the pulp, giving a pH of 9.6. Sodium
cyanide and zinc sulphate were used in combina-
tion as depressants for the sphalerite. Potassium
ethyl xanthate and cresylic acid were used as col-
lector and frother respectively for the flotation
of the galena. Following the lead roughing, the
pulp was conditioned with copper sulphate in order
to activate the sphalerite. Ethyl xanthate and
cresylic acid were used for collection of the spha-
lerite and for the production of a good froth.

So far the flotation results are normal.
The next material to be collected is calcium flu-
oride. Unfortunately the gangue consists of cal-
cite and quartz, and it is difficult to separate
two minerals having a common metal ion, in this
case fluorite and calcite.

This problem may be attacked through the
negative ion. Calcium carbonate is a highly re-
active compound, but calcium fluoride has a relat-
ively low reactivity. Hence, if we add sodium
silicate to a mixture of fluorite and calcite, we
would expect little or no reaction with the first
named mineral, but the possibility of a reaction
with the calcite thus :-

$$CaCO_3 + Na_4\ SiO_4 \ \ldots\ldots> \ Ca \begin{cases} SiO_4 \\ \\ SiO_4 \end{cases} + 2Na_2CO_3$$
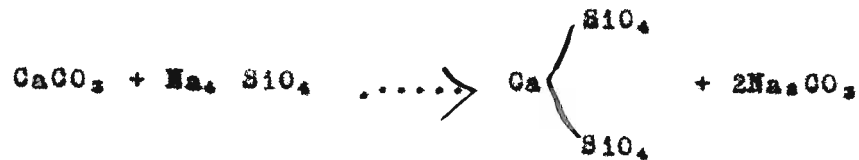
This reaction proceeds as shown, either by chemical metathesis or by adsorption. The silicate coating is polar (and hence wettable by water) but is not particularly stable. It may be stabilized by the addition of copper sulphate, followed by the addition of a collector for the fluorite. Oleic acid is a collector for fluorite.

This principle was utilized in the separation of the fluorite from the lead-zinc tailings. In this first test the separation of the fluorite was very satisfactory. The zinc-lead separation was not particularly good, however, so a number of experiments were made to ascertain whether the results could be improved.

Two final tests were made which gave excellent product. The flotation data for the final test follow :

(A) Weight of ore = 200 gms. Mesh -100

Volume of water used = 600 cc.

Pulp dilution = $\dfrac{\text{Weight of liquid}}{\text{Weight of solids}} = \dfrac{600}{200} = \dfrac{3}{1}$

(A) Percent solids = $\dfrac{\text{Weight of solids}}{\text{Total weight of pulp}} \times 100$

$= \dfrac{200}{800} = 25\%.$

Pulp consistency = $\dfrac{\text{Volume of liquid}}{\text{Volume of solids}} = \dfrac{600}{45.5}$

$= \dfrac{13}{1}$

(B) Primary crushing and grinding :-

Laboratory Jaw Crusher.

Laboratory Rolls in Closed Circuit with

48 mesh Shaking Screen.

(C) Secondary Grinding :-

Abbe' pebble mill, flint pebbles, ore stage

ground with 100 mesh screen. Tap water was

used as the grinding and flotation medium.

The pH of this water = 6.8.

(D) Reagent Additions :-

(1) General Conditioning

Zinc sulphate : 0.60 lbs. per ton of ore.

Sodium cyanide : 0.80 lbs. per ton of ore.

These zinc depressants were added to the
pebble mill during grinding, this practice giving
slightly better results than when they are added
directly to the flotation cell.

Sodium carbonate (soda ash): 2 lbs. per

ton of ore. This reagent was added to the ore pulp in the cell, and a five minute conditioning period used.

Zinc sulphate   :   1.5 lbs. per ton of ore.

Sodium cyanide :   0.5 lbs. per ton of ore.

These two reagents were added after the soda ash conditioning period.

Finally 0.10 lbs. of sodium silicate per ton of ore were added.

(2) Lead circuit reagents :-

Butyl Xanthate : 0.07 lbs. per ton of ore.

Cresylic Acid : approximately 0.10 lbs. per

ton of ore.

This gave very satisfactory lead concentrates.

(3) Zinc circuit reagents :-

Following the removal of the lead concentrates, 0.03 lbs. per ton of ore of sodium silicate were added and the pulp conditioned for two minutes. One and one-half pounds of copper sulphate were used for activation of the sphalerite. No additional frother or collector was necessary. The zinc came over as a good concentrate.

(4) Fluorspar circuit :-

The calcite was depressed by adding sodium silicate (0.05 lbs. per ton of ore) and copper sulphate (0.4 lbs. per ton of ore). After a short conditioning period 0.06 lbs. per ton of ore of oleic acid was used as a frother and fluorite collector.

The reagent consumption is shown in Table (XI).

Table (XI) - Reagent Consumption in Flotation of Sulphide Fluorspar Ore.

Reagents	Lbs./ton of dry ore
Soda ash	2.00
Zinc sulphate	2.30
Sodium cyanide	1.30
Butyl xanthate	0.07
Cresylic acid	0.10
Copper sulphate	1.90
Sodium silicate	0.20
Oleic acid	0.06

Chemical analyses of the products and percentage recoveries represented by this test are given in Table (XII).

Table (XII) - Results of Flotation Concentration of Sulphide-Fluorspar Ore.

Head Sample Analysis :

Pb	2.12%
Zn	15.3
CaO	33.2
SiO$_2$	22.3

Floated Concentrates	Wt. %	Assay %				Recovery %			
		Pb	Zn	CaO	SiO$_2$ (insoluble)	Pb	Zn	CaO	SiO$_2$ (insoluble)
Lead conc.	3.0	66	0.9	Trace	-	98.3	0.15	-	-
Zinc conc.	21.9	0.1	66.4	0.4	Trace	1.0	96.5	0.3	Trace
Fluorspar conc.	38.8	0	0.25	74	0.3	-	0.59	87.0	0.6
Tailing	36.3	0.05	1.0	11.6	61.7	0.7	2.3	12.7	99.4
	100.00	2.0195	15.0	33.0	22.5	100.00	100.00	100.00	100.00

SUMMARY AND CONCLUSIONS

(1) A rather complex ore from the Cave-in-Rock district of Southern Illinois was taken for an investigation to determine whether satisfactory high-grade lead, zinc and fluorspar concentrates could be prepared.

(2) A microscopic investigation revealed the presence of the following minerals :

Galena	Quartz
Sphalerite	Pyrite
Fluorite	Barite
Calcite	Chert

(3) Dissection of the ore by float-and-sink methods, by a microscopic examination of polished sections of the ore, and by petrographic studies, showed that the galena was free at a relatively coarse size (-35 mesh). The sphalerite and fluorite were not satisfactorily liberated at sizes coarser than 65 or 100 mesh.

(4) In view of these results it was decided to use all flotation as a method of concentrating the ore. The normal reagents for zinc and lead differential flotation proved satisfactory, but the fluor-

spar concentration proved more difficult. Finally
a reagent, consisting of sodium silicate and copper
sulphate, was found to satisfactorily depress the
calcite and at the same time permit the collection
and flotation of the fluorite with oleic acid.

(5) In the final analysis very good lead,
zinc and fluorspar concentrates were prepared. The
lead concentrates contained 66% lead and represented
a 98.5% recovery of the metal. The zinc concentrates
contained 66.4% zinc and represented a 96.5% recov-
ery. The fluorspar concentrates were high grade,
containing no lead and just a trace of zinc. Due to
the analytical difficulties involved, chemical analy-
ses of the fluorspar concentrates for fluorine were
not made, and a satisfactory recovery cannot be
assigned.

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