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# PHYSICAL PROPERTIES OF HANFORD METAL WASTE

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CHEMICAL TECHNOLOGY DIVISION

LABORATORY SECTION

# PHYSICAL PROPERTIES OF HANFORD METAL WASTE

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|---|---|
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## 1.0 Abstract

Several physical properties of Hanford metal wastes are reported. This constitutes part of the preliminary data required to scope design on a feed preparation program for the tributyl phosphate metal waste recovery process at Hanford.

## 2.0 Introduction

The slurrying, pumping, settling, and dissolving operations, incidental to the preparation of a TBP process feed, require information on a number of physical and chemical properties of the wastes involved. The work reported here was initiated to provide such necessary data as could be contemplated at the outset.

## 3.0 Summary

The Hanford metal wastes have been found to fall roughly into four categories:

(a) Supernate - the liquid waste

(b) Hard sludge - dense agglomerates of poorly defined crystalline carbonates approximating the hardness of soft blackboard chalk.

(c) Soft sludge - an easily slurried semi-solid consisting chiefly of needle-like phosphates.

(d) Recombined sludge - a representative sample of the solid wastes as received from Hanford, shown to be a mixture of hard and soft sludges in the ratio 2/3 by weight.

The density of supernate, in the temperature range 24 - 74°C, varied from 1.130 to 1.103 g/ml. Hard sludge density averaged 3.0 g/ml and that of soft sludge averaged 1.84 g/ml.

The consistency, or apparent viscosity, as a function of temperature, shear rate, and solids content was measured individually on slurries of

Summary (continued)

recombined, soft, and hard sludges using supernate as the suspending medium.

Settling rates were also run on these three slurries as a function of solids content.

## 4.0 Classification of Hanford Metal Waste

The metal wastes from Hanford tank 101-U used in these experiments were sampled from a carrier containing 20-30 liters of sludge and about 200 liters of supernatant liquid. The wastes contained can be divided into four rather distinct categories:

(a) Supernate - the clear supernatant liquid.

(b) Soft sludge - an easily slurried solid consisting chiefly of a uranyl phosphate having a definite needle-like structure.

(c) Hard sludge - dense, hard agglomerate masses of crystalline carbonate material. The crystals are all imperfectly formed.

(d) Recombined sludge - a composite sludge calculated to be representative of the sludge present in the large carrier. The two sludge types were combined in the ratio, 2 parts by weight of hard sludge to 3 parts by weight of soft sludge. This ratio

Classification of Hanford Metal Waste (continued)

was based on the uranium analyses of the individual varieties and the overall sludge carrier analysis after supernate was removed and the whole sludge sample dissolved.

Each property studied is reported separately and the work done on any one material is discussed under the heading of the property in question.

5.0 Density Determinations

Hard sludge density was measured at room temperature by liquid displacement in a graduated cylinder. Supernate was the displacement liquid employed. An average density of 3.0 g/ml. was obtained (Table I).

Soft Sludge density was measured on material which passed an 8 mesh screen to remove the gross lumps of hard sludge. A sample of this was centrifuged thirty minutes at top speed in an International clinical centrifuge and the supernatant liquid removed before weighing. The sludge was found to have a density of 1.84 g/ml. (Table II).

Supernate density was measured as a function of temperature using an Ostwalt-Sprengel type pycnometer. (Table III and Figure I). Temperature was regulated by a Precision Scientific Company oil bath to $\pm$ 0.05°C.

## 6.0 Viscosity and Consistency Measurements

6.1 Supernate viscosities The viscosity of supernate as a function of temperature was measured by comparison with water using a Fenske-Ostwalt viscosimeter (Table IV and Figure II). Thermostating was done in an oil bath regulated to $\pm$ 0.05°C.

In addition to measurements on supernate as obtained from Hanford, it was considered desirable to concentrate a sample to 80.5% of its volume for further study. The concentration was carried out at room temperature in a suction flask fitted with a one-hole stopper carrying a short length of fine capillary tubing through which filtered air was drawn such that the air stream impinged on the liquid surface. The semi-log plot (log $\eta$ vs 1/T) is very nearly linear for the original supernate, which means that the temperature dependence of viscosity is of the form,

$$\eta = \eta_0 \, {}^{m/T}$$

6.2 Apparent Viscosities (Consistencies) of Sludges

Apparent viscosities were measured using a Brookfield Synchro-electric Viscometer, Model LVF. It provided for measurements to be taken at four different spindle speeds equivalent to four different shear rates. The spindle speeds provided by this instrument were 6, 12, 30, and 60 rpm. Consistency data (Tables V and VI; Figure III, IV), (both up and down curves) were taken on both soft sludge and recombined sludge. The variation of the parameters, temperature and solids content, gave rise to families of con-

Apparent Viscosities (consistencies) of Sludges (continued)

sistency curves, that is, apparent viscosity plotted against shear rate.

A measurement was made as follows: The instrument was turned on at its slowest spindle speed after insertion to a prescribed depth in the sample. It was allowed to run for 30 seconds and a reading taken as quickly as possible, stopping if necessary. The speed was then increased to the next higher value and the process repeated until the maximum speed was attained. The down-curve was then taken immediately by reversing the order of speed selection.

In every case the viscosity decreased sharply with increasing shear rate. This indicated that a high speed stirrer of the "Lightnin" type would be preferable to a slow moving paddle for stirring these slurries.

### 6.3 Consistency of Hard Sludge

Hardness or consistency measurements in the usual sense were nearly impossible due to the difficulty in preparing or even securing a suitable sample. However, a measurement which would provide some idea of comparative consistency of hard sludge was considered desirable.

Such a comparison was made by running penetration tests on the sludge (Table VII) and various other familiar materials such as chalk, hard paraffin wax, and cake soaps.

The samples of hard sludge were clamped in a ringstand clamp and firmly held down on the protected penetrometer table.

Consistency of Hard Sludge (continued)

A spot was then scraped sufficiently flat to enable one to zero the needle on the surface. Several trials were made at various points on this prepared surface.

The instrument used as the "Precision" Universal Penetrometer fitted with a standard A.S.T.M. needle.

A reading was taken by loading the needle with suitable weights, bring the needle to the scraped surface of the sample, and the releasing the needle to allow it to penetrate the sample for a timed interval. Depth of penetration was then read off the dial provided for that purpose.

6.4 Milling of Hard Sludge

One attempt was made to determine any difficulty which might be encountered in grinding hard sludge. This was carried out in a cylindrical stainless steel ball mill about 5 1/2" in diameter x 2 1/2" long, containing 100-150 1/2" steel balls. It was charged with approximately 15 g of hard sludge averaging 1.5 cm in diameter. About 10 ml of supernate was also added to make a slurry, thus avoiding a dusting problem. The mill was rotated at 115 rpm for 1/2 hour. At the end of this time there remained three pieces about 2 mm in diameter.

The slurry resulting from this treatment had changed in color from bright lemon yellow to a dingy greenish yellow color, probably due to contamination by finely divided iron from the balls. The method was

Milling of Hard Sludge (continued)

abandoned as a method of grinding sludge for the laboratory tests because of the iron contamination.

## 7.0 Settling Rate Determinations

Settling rates were measured on slurries of hard, soft, and recombined sludges dispersed in supernate. They were determined at different solids contents, all at about 25°C.

The method of analysis for solids content throughout this work consisted of a thirty minute centrifugation of a measured volume of slurry. From the volume of the solids so obtained the solids content (expressed here as volume percent) was calculated.

The settling rates were measured by shaking the slurry in a stoppered graduated cylinder and noting the decreasing solids level periodically. The solids level was sharply defined except for initial readings on slurries of low solids content. The supernate by the same token was quite clear even at the sludge boundary.

The hard sludge was prepared for these measurements by grinding in a mortar and pestle with a little supernate.

The data contained in Tables VIII through X, inclusive, have been expressed graphically in two different ways. (1) The settled volume of the sludge (adjusted to a starting volume of 100 ml) as a function of settling time (Figures V - VII inclusive). (2) The uranium concentration

Settling Rate Determinations (continued)

in the settled portion of the total sludge sample as a function of time (Figures VIII - X inclusive). In this calculation, the uranium in the supernate is also included. The equipment and actual sludge volumes used in these experiments are summarized in Table XI.

## 8.0 Microscopic Examination of Sludges

Figures XI and XII show photomicrographs of soft and hard sludges, respectively. They represent a magnification of about 750 X. The soft sludge was made into a thin slurry and a microscope slide smear made from it. It was necessary to crush the hard sludge with a mortar and pestle in such a manner that it would break up individual crystals as little as possible. A smear was then made of a thin suspension of the crushed solid in supernate.

Soft sludge needles measured about 20 - 30 $\mu$ in length with an average diameter of about 1.5 $\mu$. Hard sludge was crystalline in appearance but few well defined crystals which permit classification can be located.

A comparison of these pictures leads to the conclusion that hard and soft sludges in all probability represent accumulations of distinct compounds. Further work on chemical identification of these species is contemplated.

C. E. Schilling

C. E. Schilling

Table I

DENSITY OF HARD SLUDGE

| Sample No. | $d_{25°}$ |
|---|---|
| 1 | 2.9 |
| 2 | 2.9 |
| 3 | 3.3 |
| 4 | 3.1 |
| Average | 3.0 |

Table II

DENSITY OF SOFT SLUDGE

| Sample No. | 25° |
|---|---|
| 1 | 1.81 |
| 2 | 1.87 |
| 3 | 1.86 |
| 4 | 1.84 |
| Average | 1.84 |

Table III

DENSITY OF SUPERNATE AS A FUNCTION OF TEMPERATURE

| Temperature(°C) | Density (g/ml) |
|---|---|
| 24.3 | 1.130 |
| 49.3 | 1.119 |
| 73.9 | 1.103 |

Table V

Apparent Viscosity of Soft Sludge As a Function of

Shear Rate For Various Solids

Contents

| Shear rate (rpm) | Apparent Viscosity (Centipoises) | | |
|---|---|---|---|
| | 74.5% Total Solids 20°C Spindle No. 3 | 58.4% Total Solids 20.6°C Spindle No. 2 | 20.5% Total Solids 24.0°C Spindle No. 1 |
| 6 | 2900 | 770 | 38.0 |
| 12 | 2450 | 495 | 29.0 |
| 30 | 2068 | 308 | 18.4 |
| 60 | 1568 | 208 | 12.8 |
| 30 | 2000 | 360 | 19.0 |
| 12 | 2310 | 725 | 33.0 |
| 6 | 2460 | 1170 | 48.0 |

[redacted]

Table VI

Apparent Viscosity of Soft Sludge As a Function of Shear Rate and Temperature

74.5% Total Solids: Spindle No. 3

| Shear rate (rpm) | Apparent Viscosity (cps) | |
|---|---|---|
| | 20°C | 59°C |
| 6 | 2900 | 1520 |
| 12 | 2450 | 1260 |
| 30 | 2068 | 1136 |
| 60 | 1568 | 968 |
| 30 | 2000 | 1076 |
| 12 | 2310 | 1110 |
| 6 | 2460 | 1160 |

Table VII

Consistency of Hard Sludge

Instrument used: Precision Scientific Company Universal Penetrometer fitted with a standard A.S.T.M. needle.

Duration of penetration - 20 seconds at 25°C

| Sample | Needle loading (g) | Penetration (mm.) |
|---|---|---|
| Hard Sludge #1 | 100 | 2.0 |
| | 200 | 1.3 |
| | 200 | 1.4 |
| Hard Sludge #2 | 400 | 1.7 |
| | 400 | 0.4 |
| | 700 | 0.7 |
| Air dried Colgate cake soap | 200 | 2.8 |
| Lava soap | 200 | 3.0 |
| Hard paraffin wax, mp: 60-2°C | 200 | 2.4 |
| Blackboard chalk | 200 | 0.7 |
| | 400 | 1.3 |
| | 700 | 2.2 |

Table VIII

Settling Rate of Soft Sludge As a Function of Solids Content

Temperature: 25°C

| Time (Min.) | 54.6 vol. % solids | | 25.5 vol. % solids | |
|---|---|---|---|---|
| | U conc. in Sludge (g/l) | Sludge Vol. (ml) | U conc. in Sludge (g/l) | Sludge vol. (ml) |
| 0 | 227 | 100 | 117 | 100 |
| 15 | | | 138 | 82.2 |
| 20 | 282 | 79.2 | | |
| 40 | 296 | 75.0 | 202 | 53.2 |
| 60 | 305 | 72.8 | | |
| 70 | | | 229 | 46.4 |
| 100 | | | 249 | 42.3 |
| 110 | 307 | 72.3 | | |
| 200 | | | 269 | 28.9 |
| 220 | 308 | 71.8 | | |
| 400 | 308 | 71.8 | | |
| 420 | | | 273 | 38.3 |
| 1400 | 308 | 71.8 | 273 | 38.3 |

Table IX

Settling Rate of Hard Sludge As a Function of Solids Content

Temperature: Approximately 25°C

| Time Min. | 26 vol. % solids | | 19 vol. % solids | | 8.0 vol. % solids | |
|---|---|---|---|---|---|---|
| | U Conc in Sludge (g/l) | Sludge vol. (ml) | U conc in Sludge (g/l) | Sludge vol. (ml) | U conc in Sludge (g/l) | Sludge vol (ml) |
| 0 | 348 | 100 | 259 | 100 | 122 | 100. |
| 15 | | | | | 166 | 69.6 |
| 20 | | | 286 | 90.0 | | |
| 40 | | | 325 | 78.4 | 268 | 41.0 |
| 60 | | | 371 | 67.2 | | |
| 70 | | | | | 305 | 35.6 |
| 100 | 462 | 74.2 | | | 332 | 32.6 |
| 110 | | | 409 | 61.4 | | |
| 150 | 506 | 67.5 | | | | |
| 190 | 511 | 66.7 | | | | |
| 200 | | | | | 385 | 27.8 |
| 220 | | | 455 | 54.8 | | |
| 400 | | | 498 | 50.0 | | |
| 420 | | | | | 441 | 24.2 |
| 1020 | 572 | 59.3 | | | | |
| 1440 | | | 537 | 46.2 | 462 | 23.0 |

## Table X

### Settling Rate of Recombined Sludge As a Function of Solids Content

Temperature 25°C

| Time Min. | 54.2 vol. % solids | | 28.6 vol. % solids | | 8.0 vol. % solids | | 5.2 vol. % solids | |
|---|---|---|---|---|---|---|---|---|
| | U conc in Sludge (g/l) | Sludge vol(ml) | U conc in Sludge (g/l) | Sludge vol(ml) | U conc in Sludge (g/l) | Sludge vol(ml) | U conc in Sludge (g/l) | Sludge vol(ml) |
| 0 | 355 | 100 | 199 | 100 | 70 | 100 | 52.6 | 100. |
| 5 | | | | | 89 | 72.3 | 59.2 | 83.0 |
| 8 | | | 205 | 96.7 | | | | |
| 10 | | | | | 115 | 52.3 | | |
| 15 | 377 | 93.8 | | | | | 103 | 39.0 |
| 20 | | | | | | | 160 | 23.0 |
| 25 | | | | | 211 | 25.8 | | |
| 32 | | | 233 | 84.0 | | | | |
| 35 | | | | | | | 240 | 14.6 |
| 36 | | | 237 | 82.4 | | | | |
| 40 | | | | | 256 | 20.9 | | |
| 45 | 398 | 88.6 | | | | | 256 | 13.6 |
| 51 | | | 263 | 73.4 | | | | |
| 60 | | | 292 | 65.6 | 281 | 18.9 | | |
| 91 | | | 324 | 58.7 | | | | |
| 100 | | | | | 312 | 16.9 | 307 | 11.2 |
| 120 | | | | | | | | |
| 155 | | | 357 | 52.9 | | | | |
| 245 | 442 | 79.2 | | | | | | |
| 260 | | | | | 358 | 14.6 | | |
| 1400 | 546 | 63.6 | 400 | 46.5 | 362 | 14.5 | | |

Table XI

Equipment Used in Sludge Settling Rate Experiments

| Sludge Type | % Solids | Graduate Size | | |
|---|---|---|---|---|
| | | Vol. (ml) | Height of graduated section (cm) | Vol. Slurry used in Expt. (ml) |
| Soft Sludge | 54.6 | 50 | 15.3 | 22 |
| | 25.5 | 50 | 15.3 | 47 |
| Hard Sludge | 26.0 | 50 | 15.3 | 27 |
| | 19.0 | 50 | 15.3 | 37 |
| | 5.0 | 100 | 19.3 | 87 |
| Recombined | 54.2 | 50 | 15.3 | 48 |
| | 28.6 | 100 | 19.3 | 91 |
| | 8.0 | 500 | 28.7 | 325 |
| | 5.2 | 500 | 28.7 | 500 |

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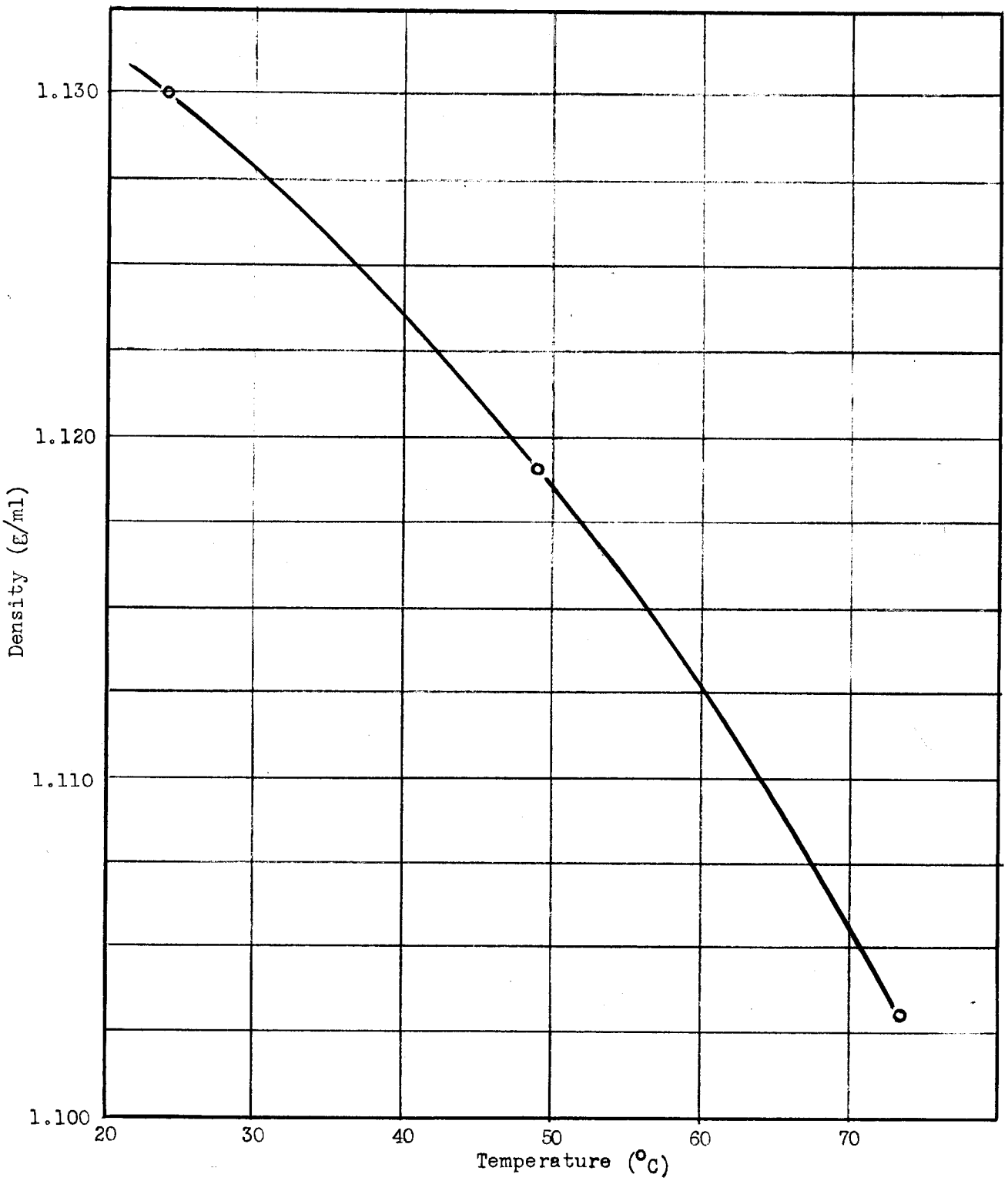
Drawing No. 9071

FIGURE I

DENSITY OF SUPERNATE AS A FUNCTION OF TEMPERATURE

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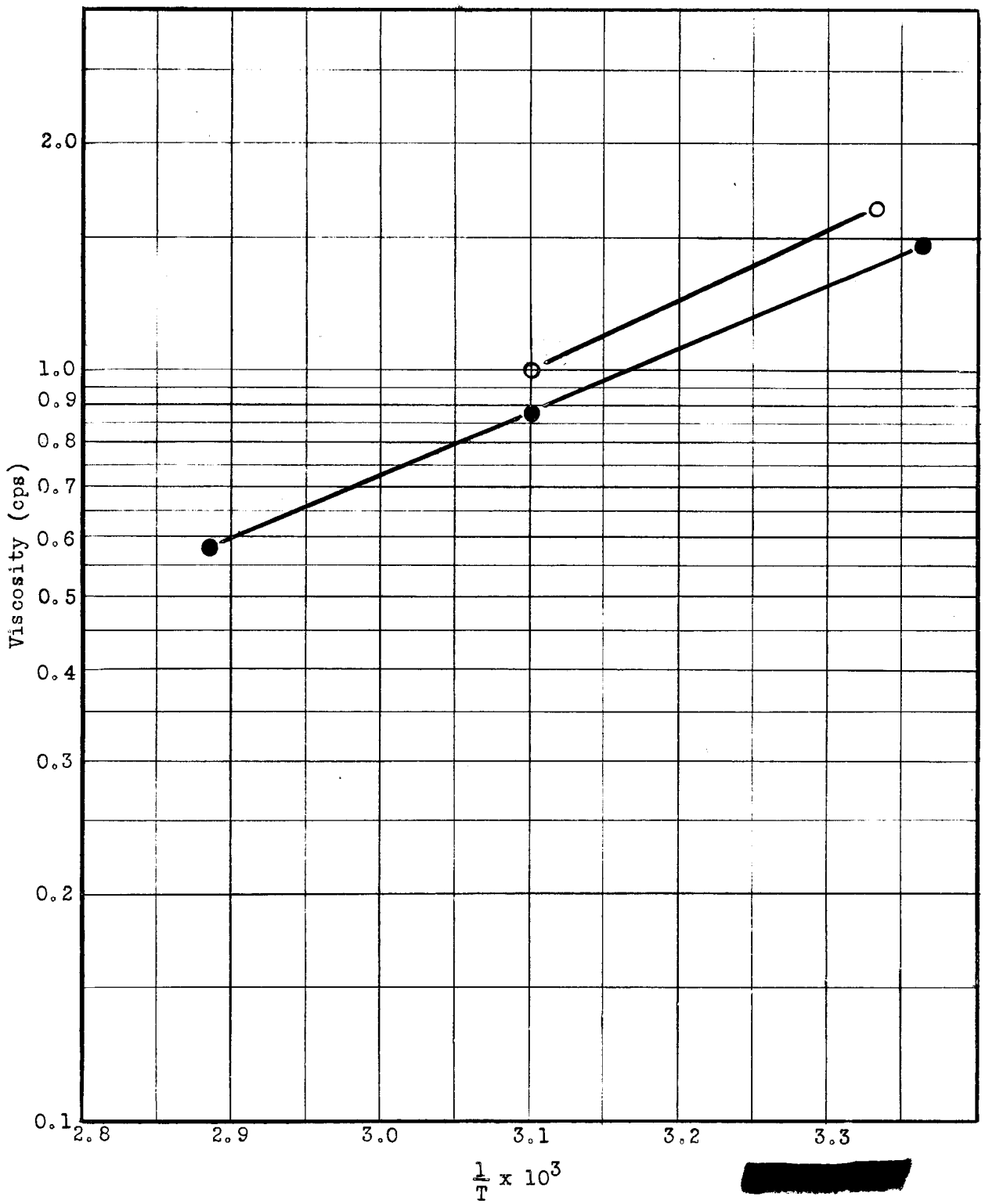
Drawing No. 9072

FIGURE II
VISCOSITY OF SUPERNATE AS A
FUNCTION OF TEMPERATURE

Code

○ 101-U Supernate Concentrated to 80.5% of its original volume.

● 101-U Supernate

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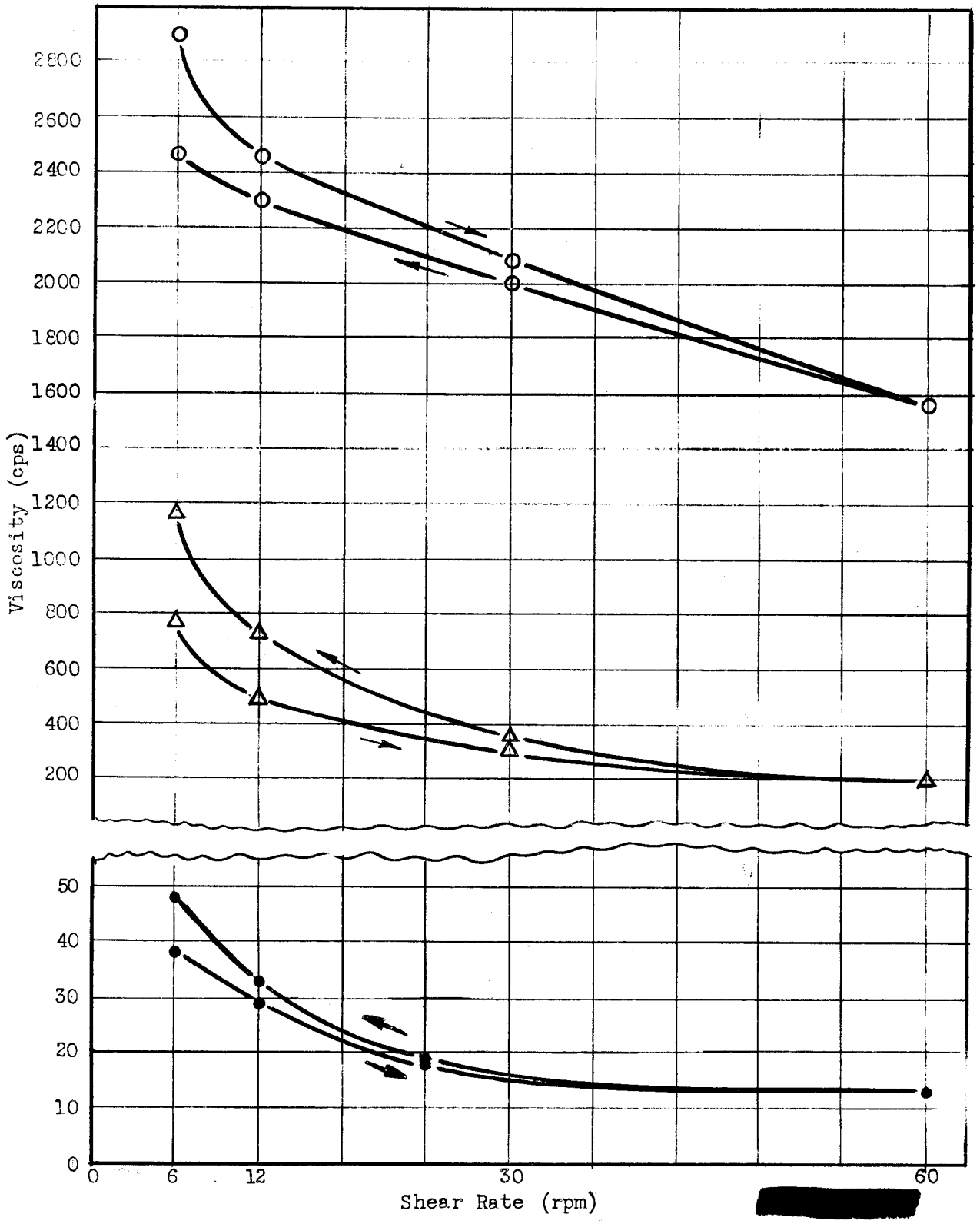
Drawing No. 9073

FIGURE III

APPARENT VISCOSITY OF SOFT SLUDGE AS A FUNCTION OF SHEAR RATE FOR VARIOUS SOLIDS CONTENTS

Temperature: ca. 20° C.

| Code | Solids Content |
|---|---|
| ○ | 74.5% |
| △ | 58.4% |
| ● | 20.5% |

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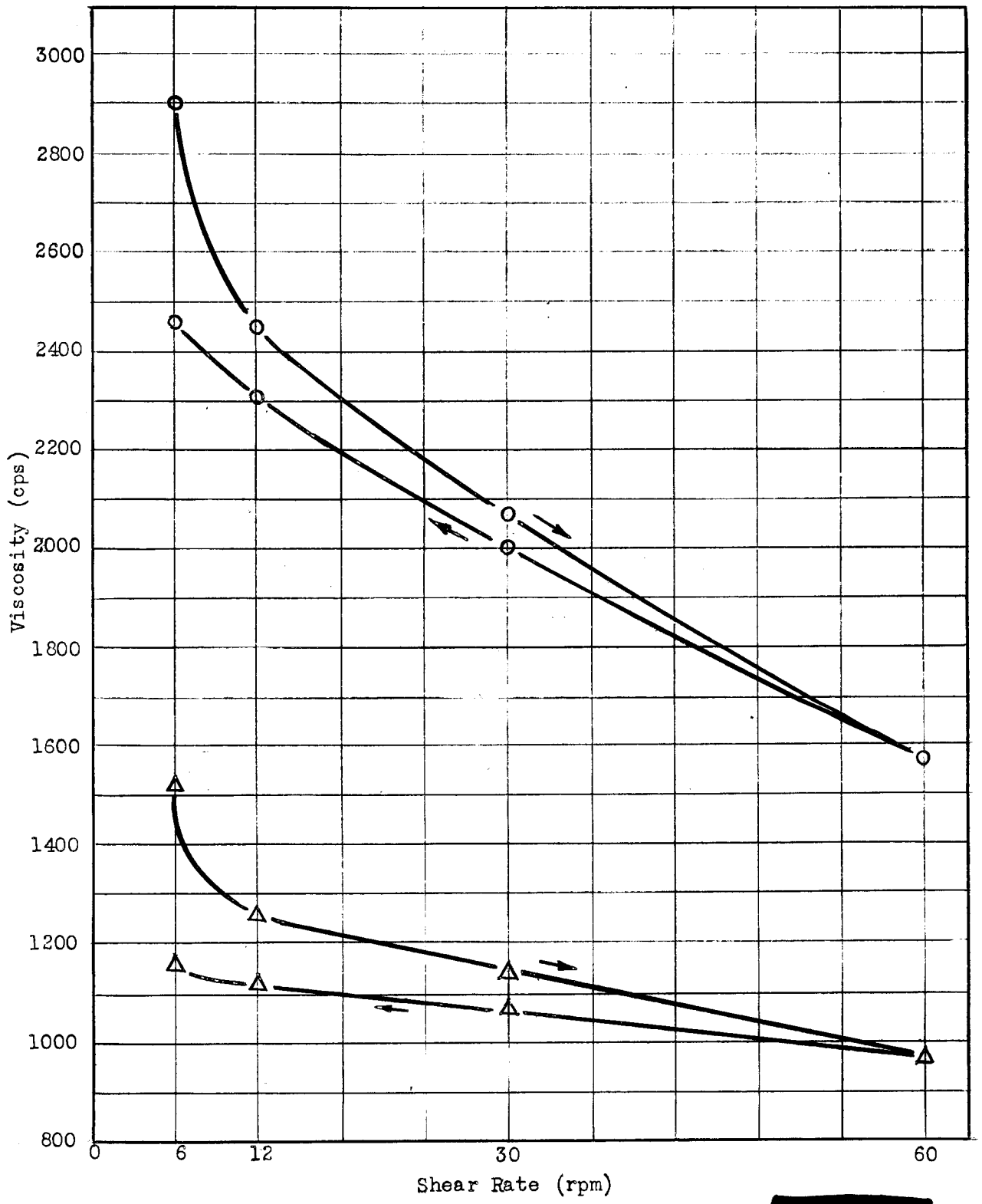
Drawing No. 9074

FIGURE IV

APPARENT VISCOSITY OF SOFT SLUDGE AS A FUNCTION OF SHEAR RATE FOR VARIOUS TEMPERATURES

Solids Content: 74.5%

| Code | Temperature °C |
|---|---|
| ○ | 20 |
| △ | 59 |

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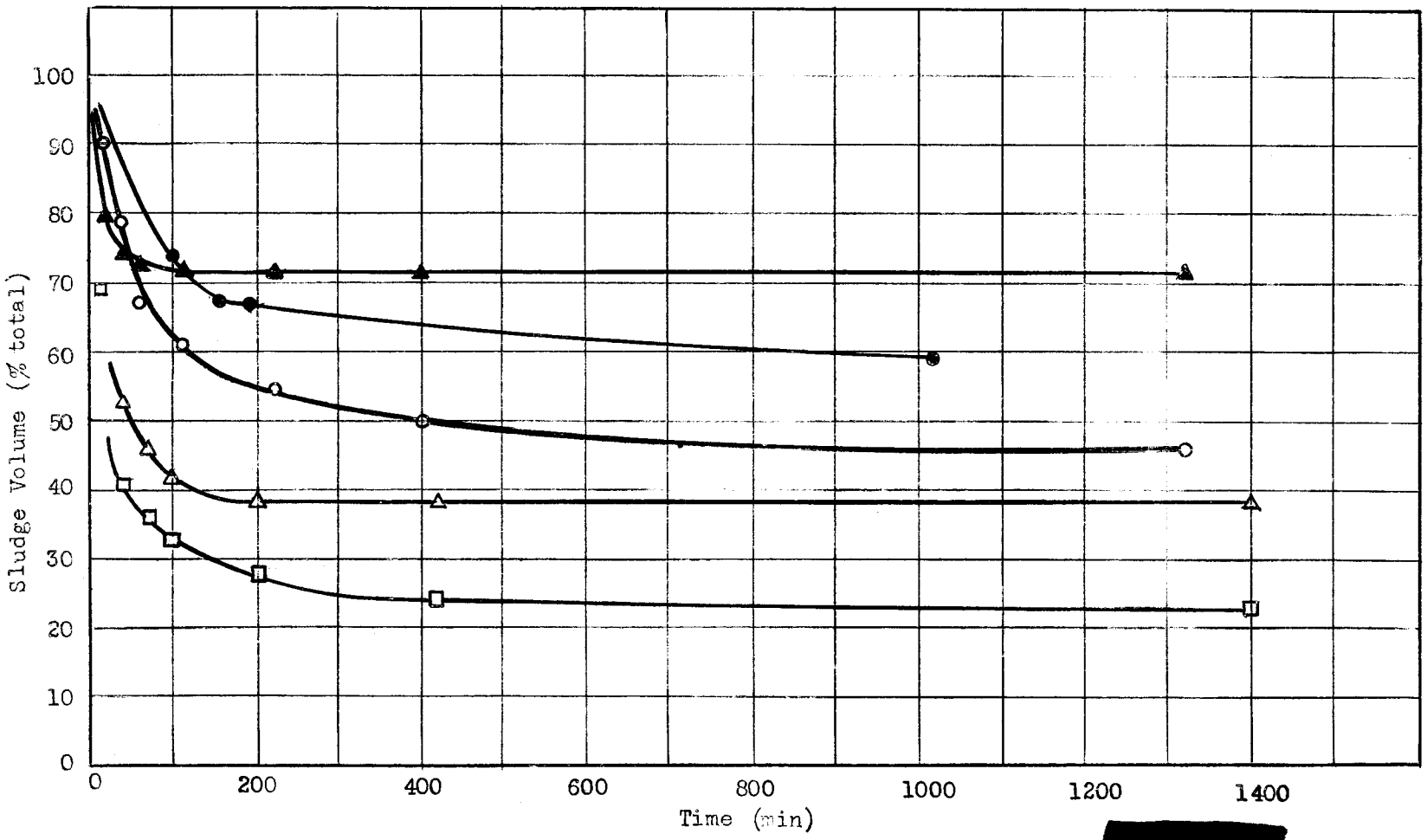
Drawing No. 9075

FIGURE V

SETTLING RATES OF SOFT AND HARD SLUDGES

AS A FUNCTION OF SOLIDS CONTENT

| Code | Vol. % solids | Sludge Type |
|---|---|---|
| ▲ | 54.6 | Soft |
| ● | 26.0 | Hard |
| ○ | 19.0 | Hard |
| △ | 25.5 | Soft |
| □ | 8.0 | Hard |

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Drawing No. 9076

FIGURE VI

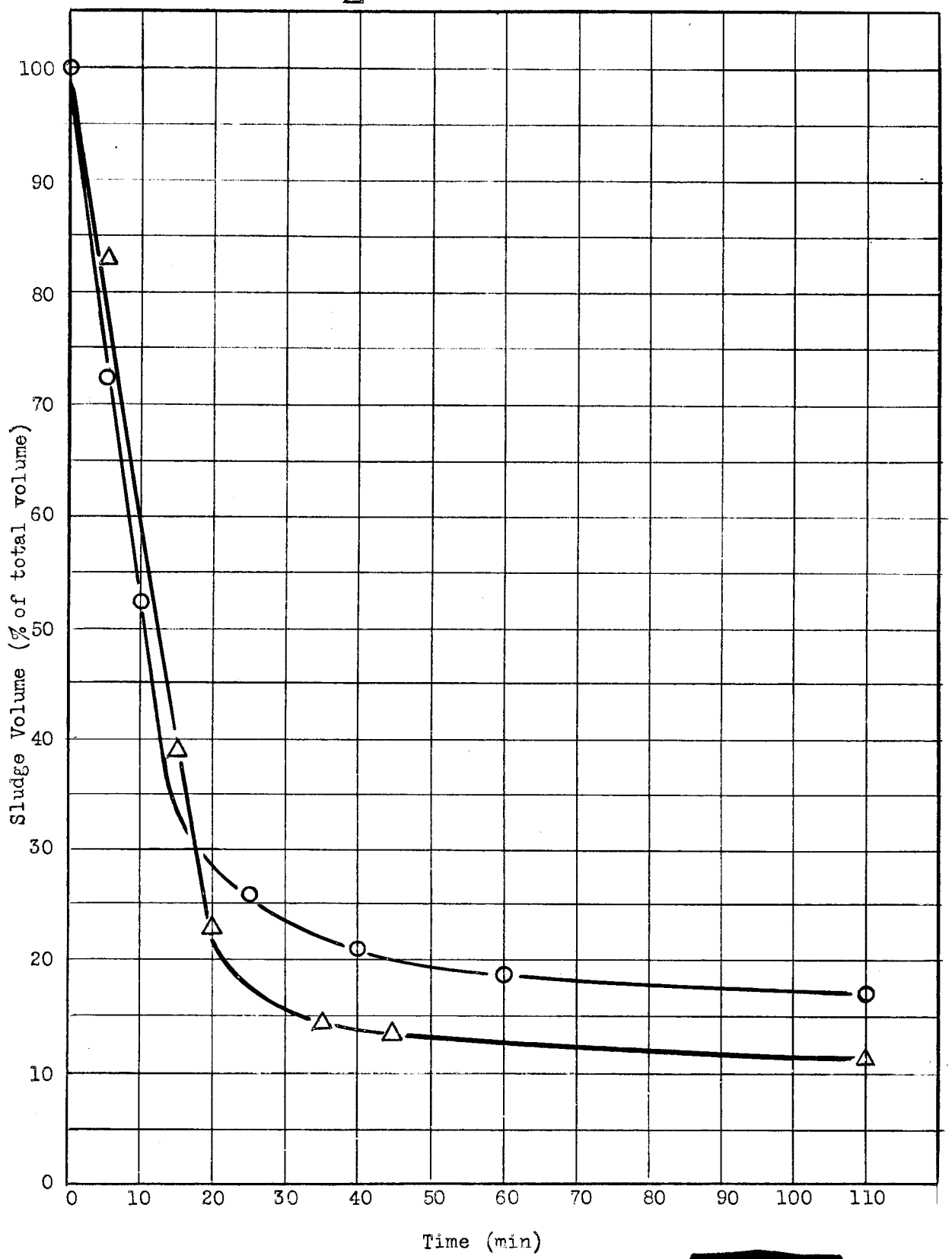
SETTLING RATE OF RECOMBINED SLUDGE

AS A FUNCTION OF SOLIDS CONTENT

Medium: Supernate

Temperature: 25° C

| Code | Volume % Solids |
|---|---|
| ○ | 8.0 |
| △ | 5.2 |

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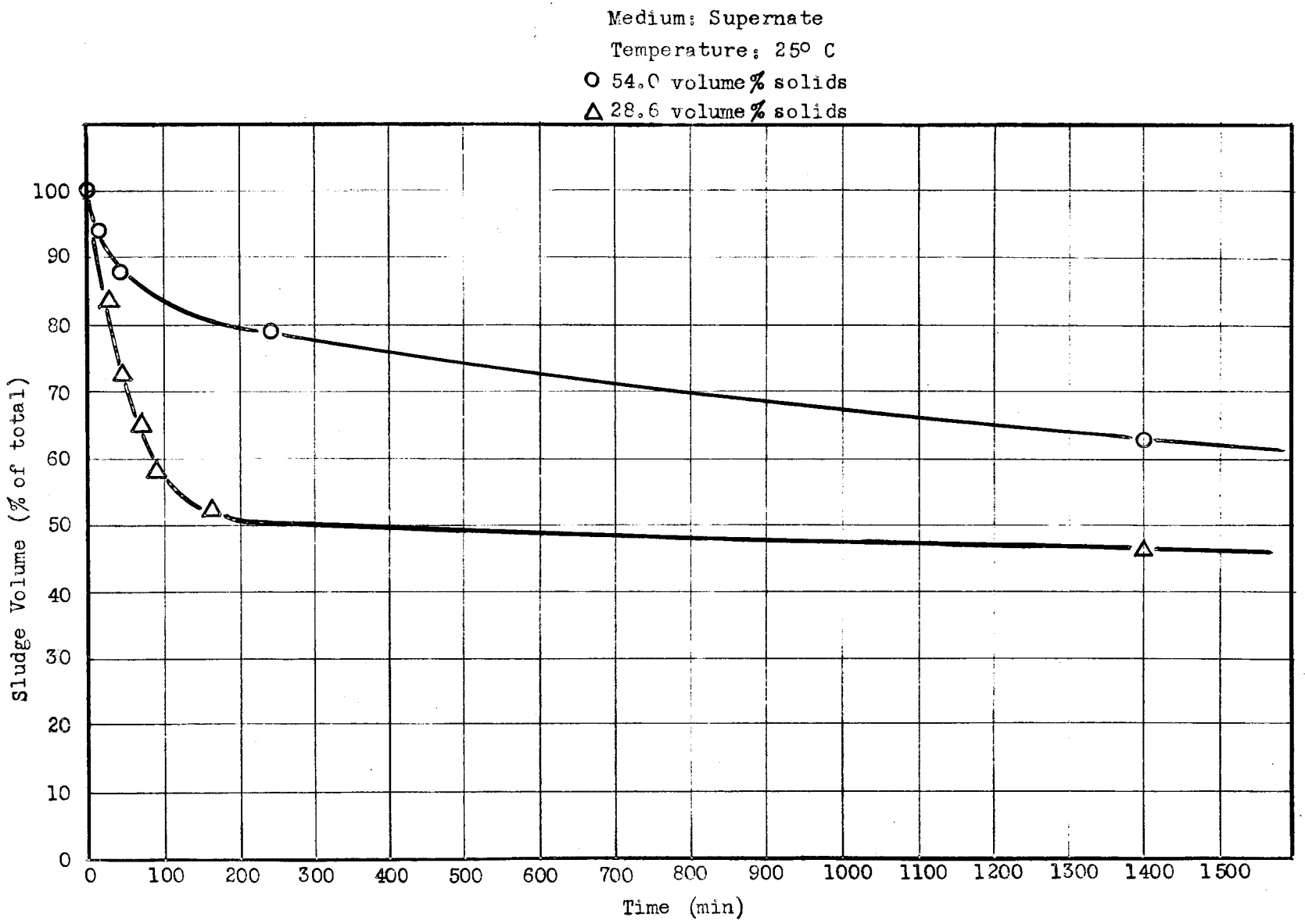
Drawing No. 9077

FIGURE VII

SETTLING RATE OF RECOMBINED SLUDGE AS A FUNCTION OF SOLIDS CONTENT



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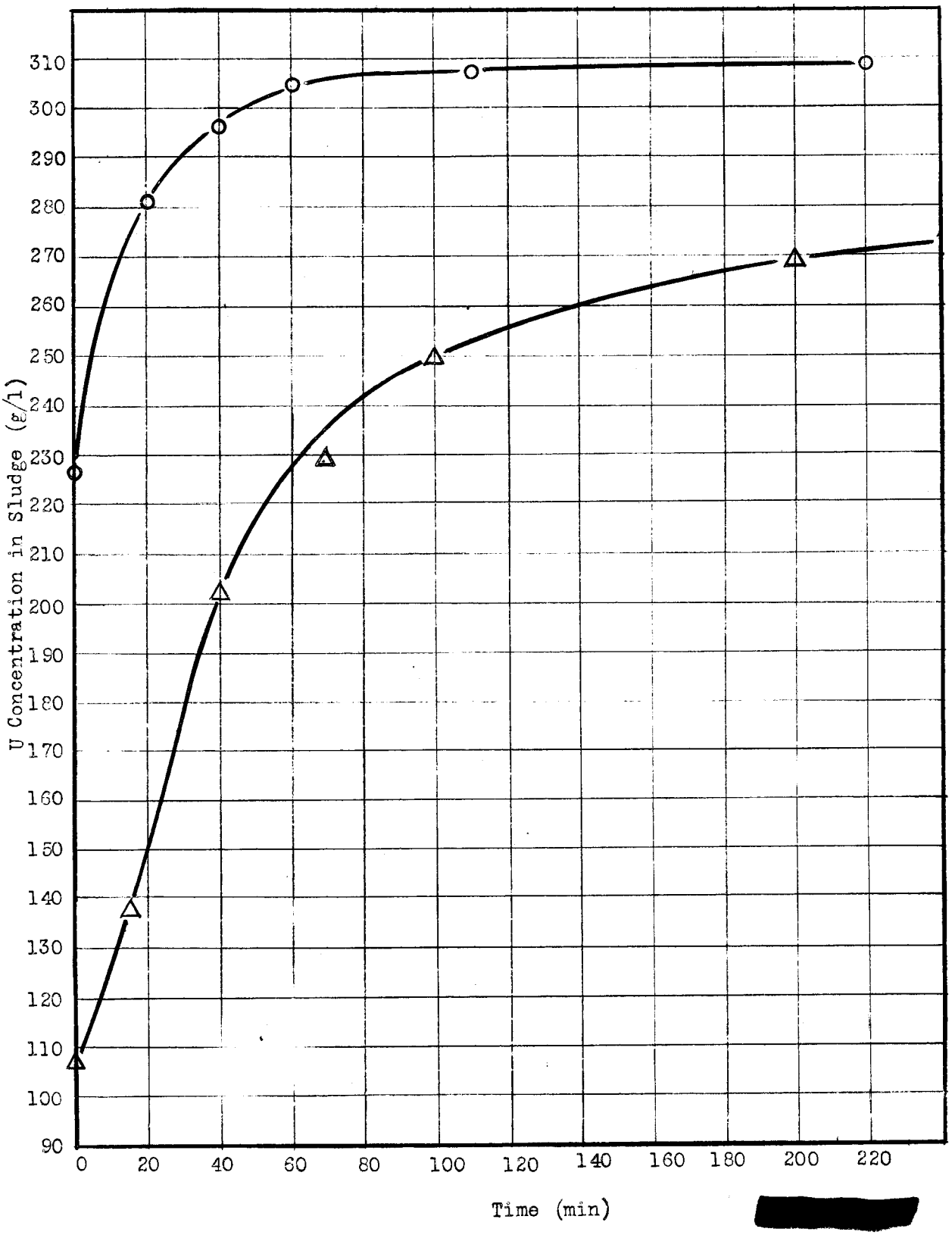
Drawing No. 9078

FIGURE VIII

VARIATION OF URANIUM CONCENTRATION IN SOFT SLUDGES AS A FUNCTION OF SETTLING TIME

Temperature: 25° C

| Code | Volume % Solids |
|---|---|
| O | 54.6 |
| △ | 25.5 |

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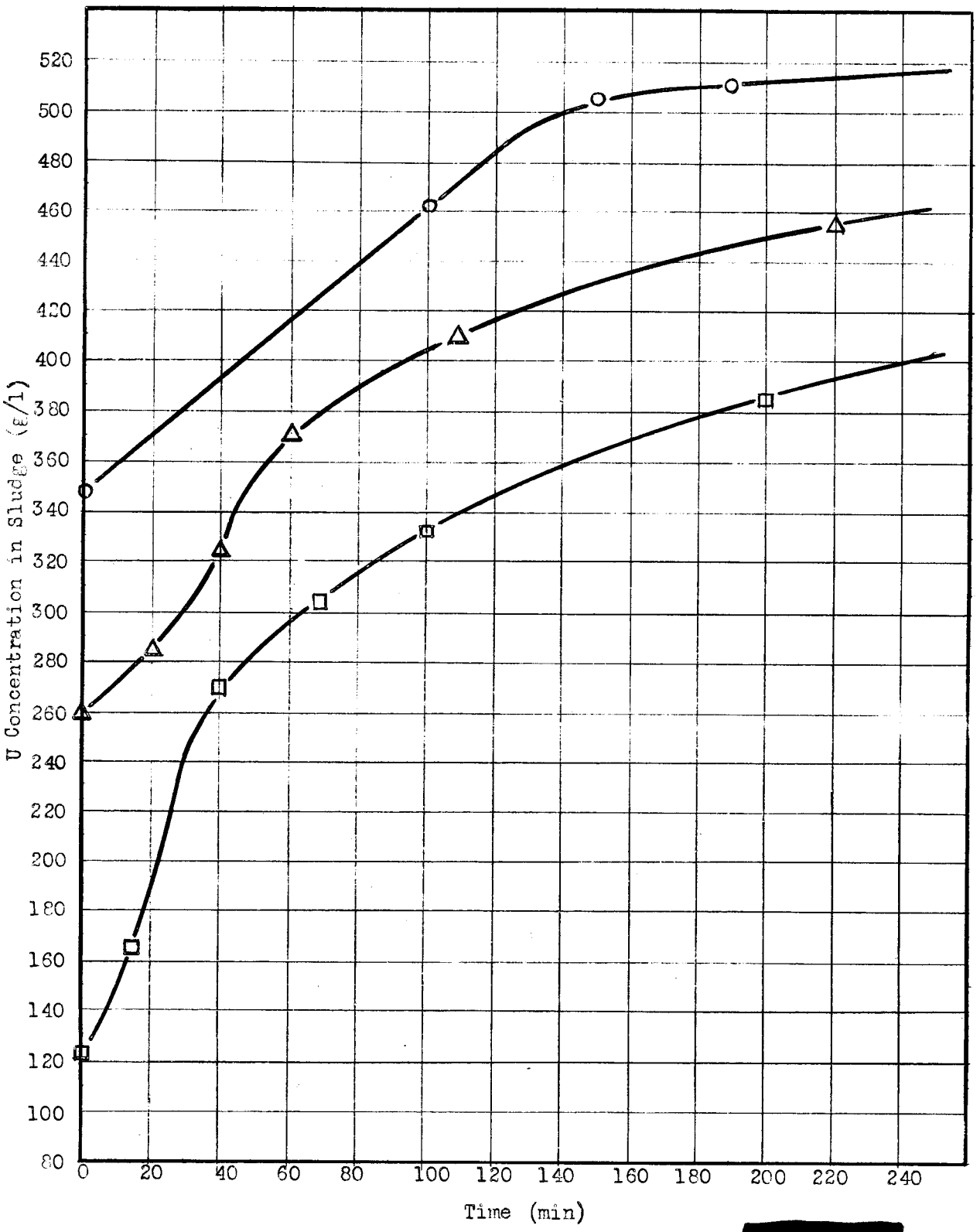
Drawing No. 9079

FIGURE IX

VARIATION OF URANIUM CONCENTRATION IN HARD SLUDGES AS A FUNCTION OF SETTLING TIME

Temperature: 25° C

| Code | Volume % Solids |
|---|---|
| ○ | 26.0 |
| △ | 19.0 |
| □ | 8.0 |

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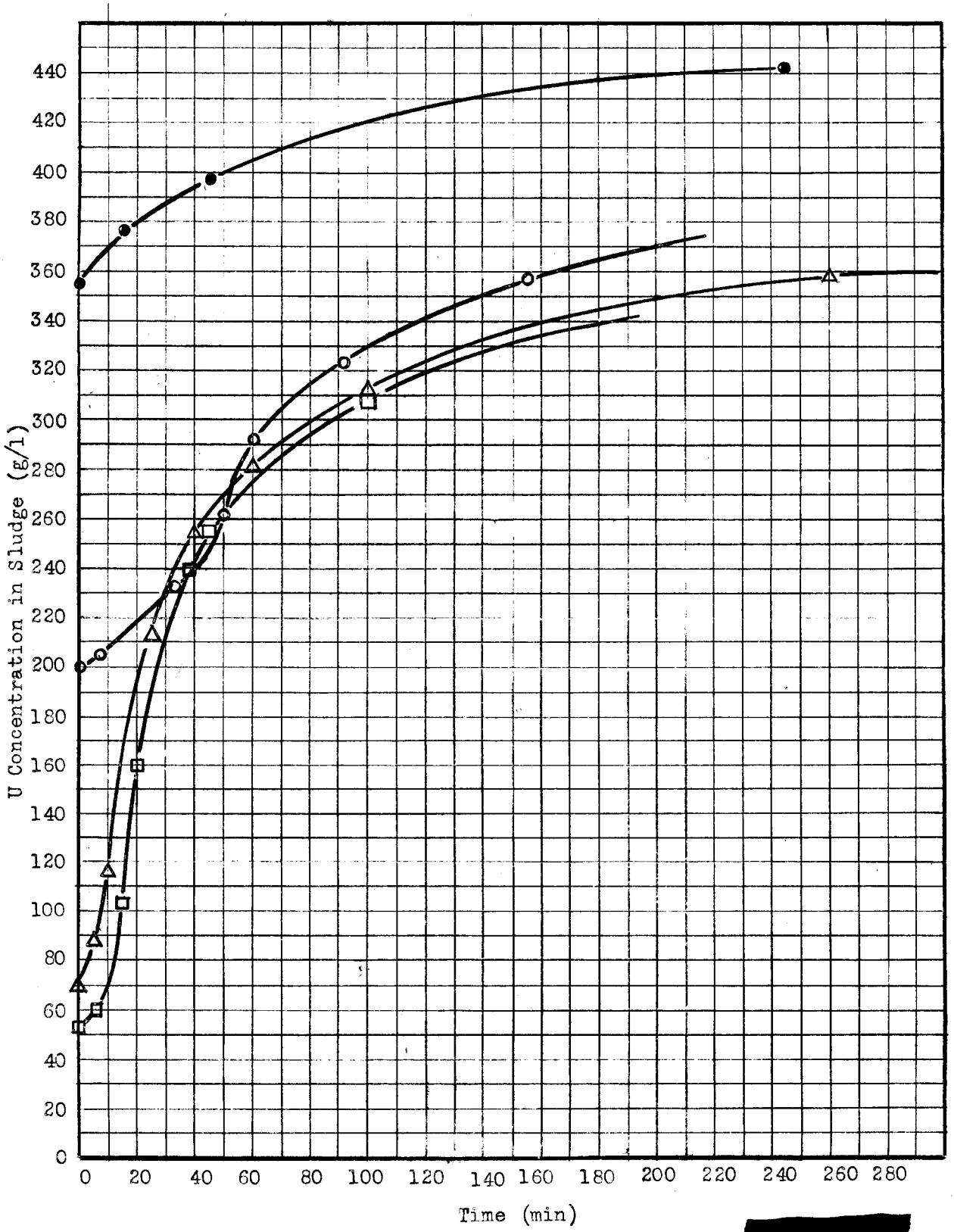
Drawing No. 9080

FIGURE X

VARIATION OF URANIUM CONCENTRATION IN RECOMBINED SLUDGES AS A FUNCTION OF SETTLING TIME

Medium: Supernate
Temperature: 25° C

| Code | Volume % Solids |
|---|---|
| ● | 54.2 |
| ○ | 28.6 |
| △ | 8.0 |
| □ | 5.2 |

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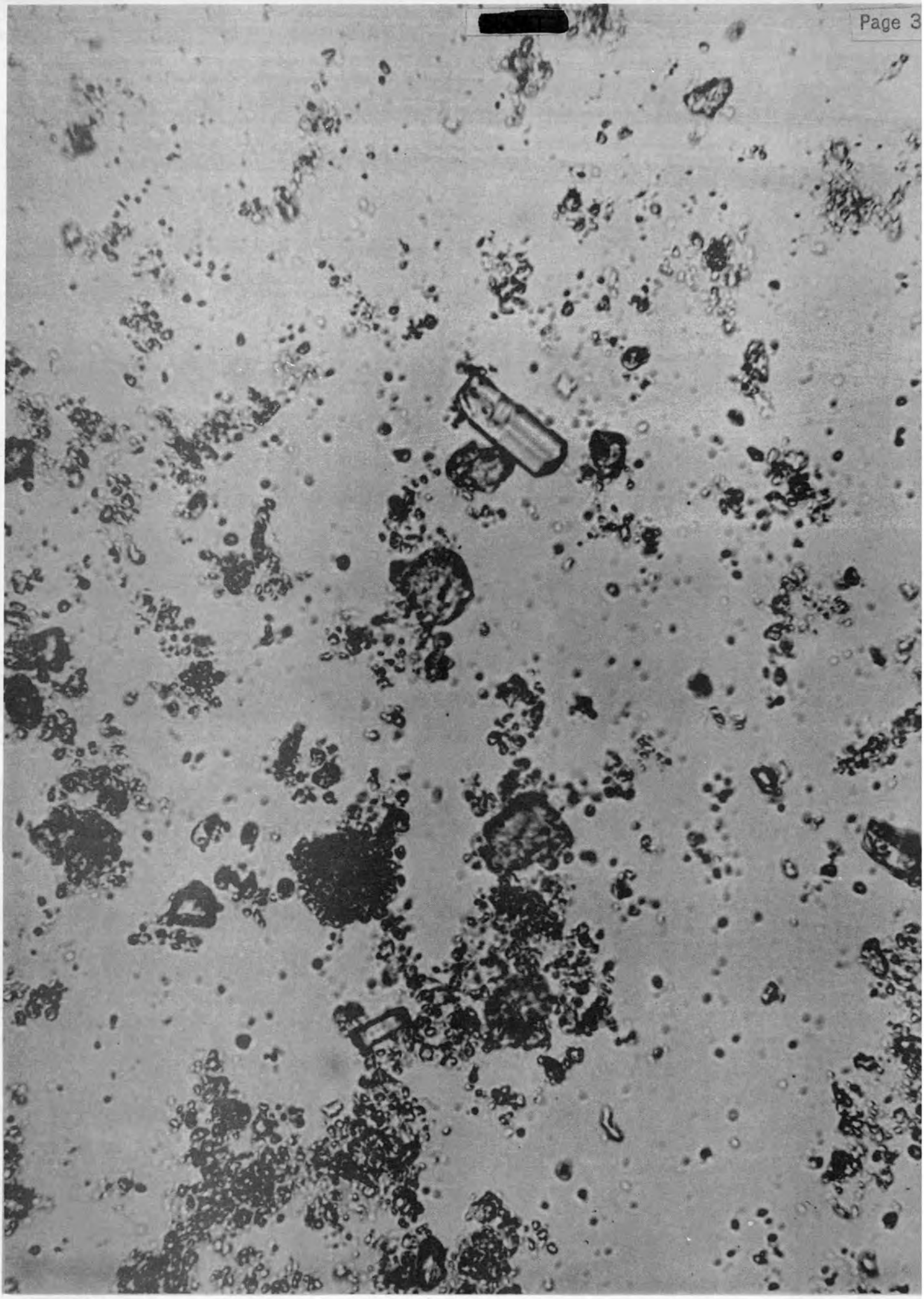

Plate M-532 USC - Hanford Sludge Crystals 750X

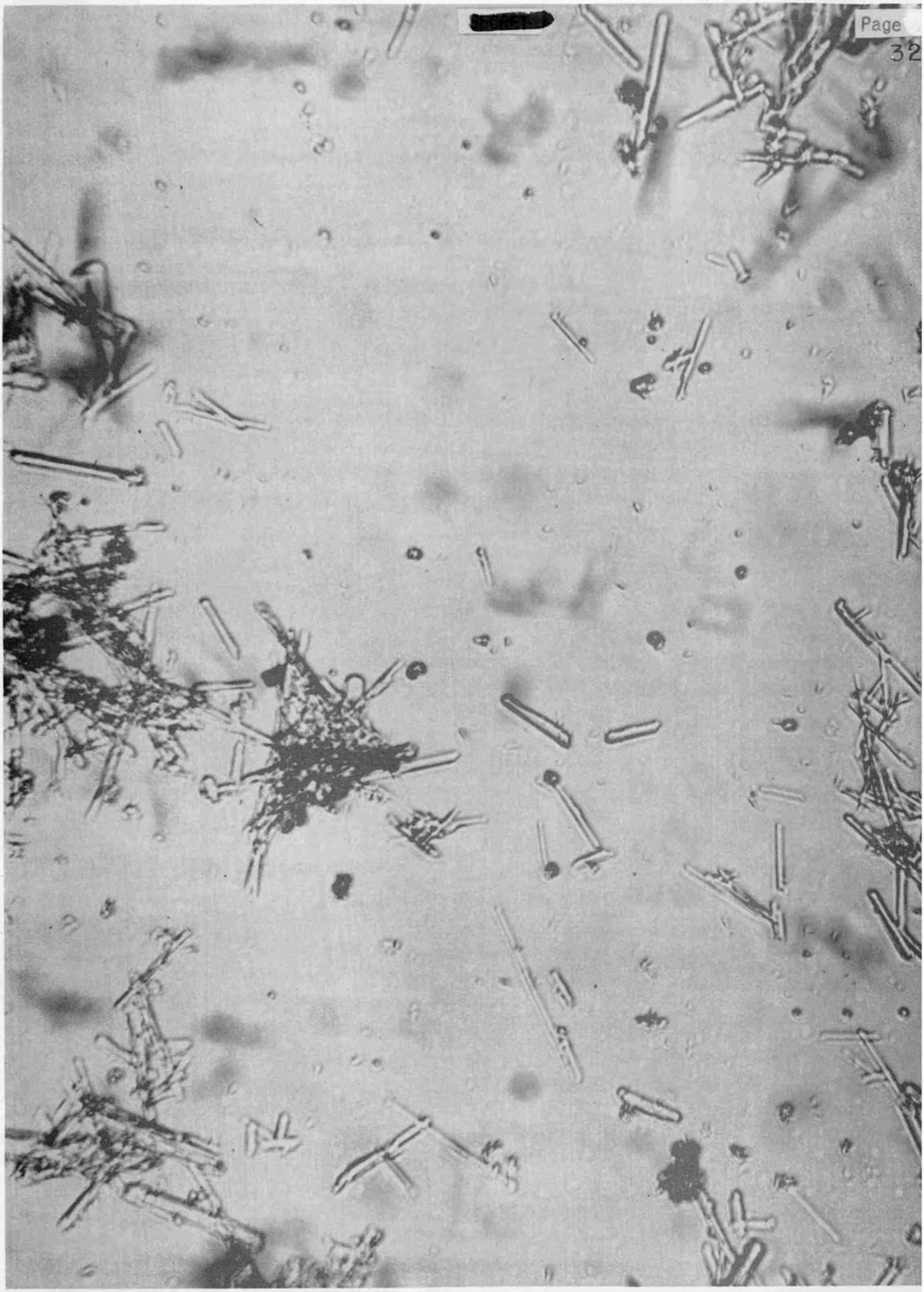

Plate M-533 USP - Hanford Sludge Crystals 750X