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URANIUM OXIDE SLURRY PUMPING EXPERIMENTS[1]

Problem Assignment No. 182 MLC 2602
(Terminal Report)

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[1] The work reported herein was initiated and directed by [redacted]
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0. Abstract

Experiments on colloid milling and pumping show that uranium trioxide, when carefully dehydrated, can be dispersed in water to form a relatively stable slurry, suitable for a homogeneous slurry pile. At temperatures considerably below those of anticipated pile operation particle size growth occurs attended by increase in settling rate and decrease in viscosity. These properties of the slurries may be strongly affected by impurities present as well as by special operating conditions.

1. Introduction

At the time when former Section C-V was made up of a portion of the Columbia group, it set forth a program of work on uranium oxide slurries for a homogeneous P-9 pile (N-193, October 25, 1943). Among other lines of work this program called for some large scale tests on the pumping of oxide slurries. The object of this phase of the work included

(a) an engineering test of the performance of a type of centrifugal pump considered desirable for a homogeneous slurry pile; and

(b) observation of significant changes in an oxide slurry with time of pumping. Changes in viscosity and settling rates are important considerations in engineering design of a slurry pile with its associated pumps and piping systems.

This long term "endurance" test to be conducted at Site B by the Technological Division, necessitated considerable work in installation. In the meantime some pumping tests have been conducted using readily available equipment. The results obtained should be valuable preliminary to the larger scale run.

2. Equipment

The apparatus for these preliminary pumping tests was built and serviced by Mr. Lyon's group in the Technological Section. Work of Section C-V was concerned with the method of preparation of the slurry, laboratory tests and interpretation of results. The apparatus consisted of a 100 gpm bronze impeller centrifugal pump connected by large iron piping to an iron tank and a return pipe leading to the intake of the pump. Valves, a sampling tube and means for control of temperature were provided. Briefly, the experiment consisted of continued circulation of a slurry at high speed for a prolonged period with periodic sampling and testing of the slurry.

3. Preparation of slurry

The uranium trioxide manufactured by the Mallinckrodt Company is a granular material which settles too rapidly to serve as slurry material without further treatment. At the time of initiation of this program it was planned to employ "micronized" oxide for slurry preparation. The micronizing treatment subjects the granular oxide to a self-impingement action by means of high velocity air streams. The average particle size of the product is of the order of 1 μ. Inasmuch as the uranium oxide must be strictly anhydrous for use in a heavy-water slurry pile, the micronizing technique must employ dry air for the operation.

Pumping Experiment No. 1 employed a slurry of micronized oxide. The results of the experiment were unsatisfactory because of rapid settling of the slurry and insufficient turbulence afforded by the system. It was considered desirable at this point to reconstruct the apparatus in order to avoid these difficulties.

The reconstruction of the apparatus involved considerable time because of more urgent work on the program of Mr. Lyon's Engineering Development Section. In the meantime another part of the slurry pile program developed some striking results. This work was directed toward the production of a relatively slowly settling slurry for use in a homogeneous exponential experiment. These results warranted some change in thinking about the whole subject of the preparation and properties of uranium oxide slurries.

3.1. Dispersing properties of UO_3

The micronized oxide when slurried with water settled much too rapidly for the projected use in the homogeneous exponential experiment. Attempts were made to disperse the particles and cause further decrease in particle size by means of a colloid mill. Various agents were added in small amounts to the slurry during the colloid mill treatment in the hope of stabilizing the dispersions, but results in this direction were not encouraging. It was noted, throughout this work, however, that the lots of micronized oxide on hand contained considerable water of hydration. Because of the necessity for employing strictly anhydrous oxide for the heavy water slurry preparation some of the material was dehydrated by heating at 300°C. This anhydrous oxide showed entirely different behavior when dispersed in water in the colloid mill. The combination of the high-speed dispersing-action of the mill and the reaction of hydration of the oxide resulted in a very slowly settling slurry. Moreover, employment of either the coarse granular oxide or the micronized variety as starting material gave the same result. These slowly settling slurries unfortunately were extremely viscous, exhibiting plastic-flow properties. This, of course, was a matter of serious concern for the projected exponential experiment. In the latter it would be necessary to handle large quantities of slurry and alter the concentration of the oxide for different runs with assurance at all times of complete homogeneity.

Since the time of these experiments, the use of an oxide slurry for the exponential experiment has been abandoned in favor of a solution of uranyl fluoride. Nevertheless this work was of value when the question of the slurry pumping experiments was reviewed. Dispersion-hydration action during colloid mill treatment of an anhydrous oxide-water suspension might conceivably occur in the pumping experiment because of the shearing action of the pump impeller. In other words, the observations with the colloid mill might represent an extreme case of what would happen under any conditions of violent agitation of the slurry. Accordingly, these considerations were born in mind in the preparation of slurry for the second pumping experiment.

Some laboratory work on oxide dispersion by colloid milling was performed shortly before the scheduled start of Pumping Experiment No. 2. Its purpose was the determination of the conditions for dehydration of a substantial quantity of the oxide to be used in the pumping experiment. At first the results did not confirm the earlier work at all, and varied in a most unpredictable manner. It became apparent that the dispersing properties of the oxide were governed by numerous factors not yet understood. That is, the degree of dehydration was not the only variable affecting the subsequent dispersing properties. Inasmuch as the anhydrous oxide is stable in the temperature range of 250-550°C, any temperature within this range may be employed for dehydration. The temperature employed, however, would affect the rate of dehydration and conceivably the physical form of the residual anhydrous oxide. Moreover, other variables such as time of dehydration at a given temperature, particle size of the oxide, thickness of layers of the material and chemical purity might be important. A thorough investigation of the effects of all of these variables has not yet been made but sufficient work has been done to indicate the following:

(a) High temperatures and long heating times result in oxides whose dispersions in water are relatively low in viscosity. This is also the case for low temperatures in the dehydration range.

(b) Intermediate temperatures and relatively short heating times give oxides whose dispersions in water are highly viscous.

(c) The viscosity of dispersions prepared from dehydrated oxides is dependent on the presence of residual nitrate. This has been shown both by correlation of nitrate analyses on heat treated oxides with viscosity of their dispersions and by the increase in viscosity of oxides dispersed in water containing added nitrate as UNH.

For use in a homogeneous slurry pile pure anhydrous oxide is necessary. Its preparation requires prolonged heat treatment of oxides prepared from UNH in order to reduce the nitrate content to an acceptable figure. Much of the work on slurries in the past has been done with relatively impure material; i.e., containing 0.15% residual UNH. Although this appears to be small, its influence on colloidal properties of dispersed oxides can be quite considerable.

4. <u>Slurry pumping run No. 2</u>

A 50 lb. lot of granular uranium trioxide was heated for 40 hours at 500°C in an oven provided with a forced draft of air. Unfortunately it was necessary, because of limitations of time and equipment, to treat this large lot of oxide in relatively thick layers. The previous exploratory work with the colloid mill had indicated that such conditions would result in relatively viscous slurries. Similarly the nitrate content of the oxide was not reduced to as low a figure as desired.

The oxide and distilled water sufficient to make a slurry containing 0.2 g U/ml were introduced into the tank of the pumping system. Because of the turbulence of the system the slurry reached a temperature of 70°C in a short time. The temperature was maintained fairly constant thereafter and evaporation losses were compensated by addition of distilled water.

The oxide became dispersed in about an hour of pumping; the slurry at this point became very viscous and showed very slow settling rate. Thus the action of the pumping system was similar to that of the colloid mill. Upon prolonged pumping the slurry was found to decrease steadily in viscosity, to increase in settling rate and as shown by the electron microscope (see report CC-2094) to increase definitely in particle size.

Pumping experiment No. 2 was imperfect in many respects. Unfortunately some losses of slurry occurred because of leaks in pump packing with consequent decrease in slurry concentration. All laboratory tests on properties of the slurry have been made on samples adjusted to a standard concentration. Pumping experiment No. 3, a repetition of No. 2, was marred for the same reason. Furthermore, corrosion of parts of the system with consequent metal pickup in the slurry raises the question of just what part electrolytes might have played in the results.

Altogether, however, some definite conclusions can be drawn from this work.

(a) Granular uranium trioxide when carefully dehydrated can be made to disperse in water to form a slurry satisfactory for the homogeneous pile. This dispersing tendency is a fundamental property of the oxide and may be exploited to make preliminary pulverizing or "micronizing" treatment unnecessary.

(b) Despite the shearing action of the pumping system a net increase in particle size occurs at the elevated temperature of the system. This is similar to the digestion of precipitates in inorganic analysis.

(c) The changes in properties of the slurry tend toward steady states after long pumping times. The final slurry, however, is sufficiently dispersed to behave satisfactorily as far as pumping is concerned.

5. <u>Suggestions for the future</u>

The slurry work has been suspended for the present but it may be reconsidered in the future. Some suggestions for further study follow. These comprise work on the colloidal phenomena associated with the uranium oxides. The influence of electrolytes should be thoroughly investigated. Experiments along this line should include preparation of uranium oxides in several different ways in order that residual impurities be of different types. These suggestions, of course, are entirely apart from much needed information on the effect of pile radiation.

6. Summary of experimental data

6.1. Viscosity

Viscosity of samples of the slurry was determined by a Stőrmer viscometer. The interpretation of viscosity figures in terms of yield value and coefficient of rigidity (A-777) was found not to apply to the present materials. A rigorous investigation of the best means of measurement and interpretation of viscosity figures has not been conducted and it has been necessary to be somewhat arbitrary in this connection. Viscosity changes, however, have been found to be so great that almost any relative method would suffice for the purpose. The figures reported below are the weights in grams required to produce a rotor speed of 750 rpm when the special container cup described in report A-777 is employed.

6.2. Settling rates

Settling rates were determined by observing the rate of massive settling of 100 ml of well shaken slurry in a 100 ml glass stoppered graduate. The initial rate of increase of supernatant liquor in ml/hr is indicated together with the ultimate settling volume of oxide as percent of initial slurry volume.

6.3. Particle size

Electron micrographs of slurry samples have been taken by Dr. Copeland's group at Illinois Institute of Technology. Statistical studies of particle size counts have been made; details may be found in special reports to the Project by Dr. Copeland. (See also report CC-2094).

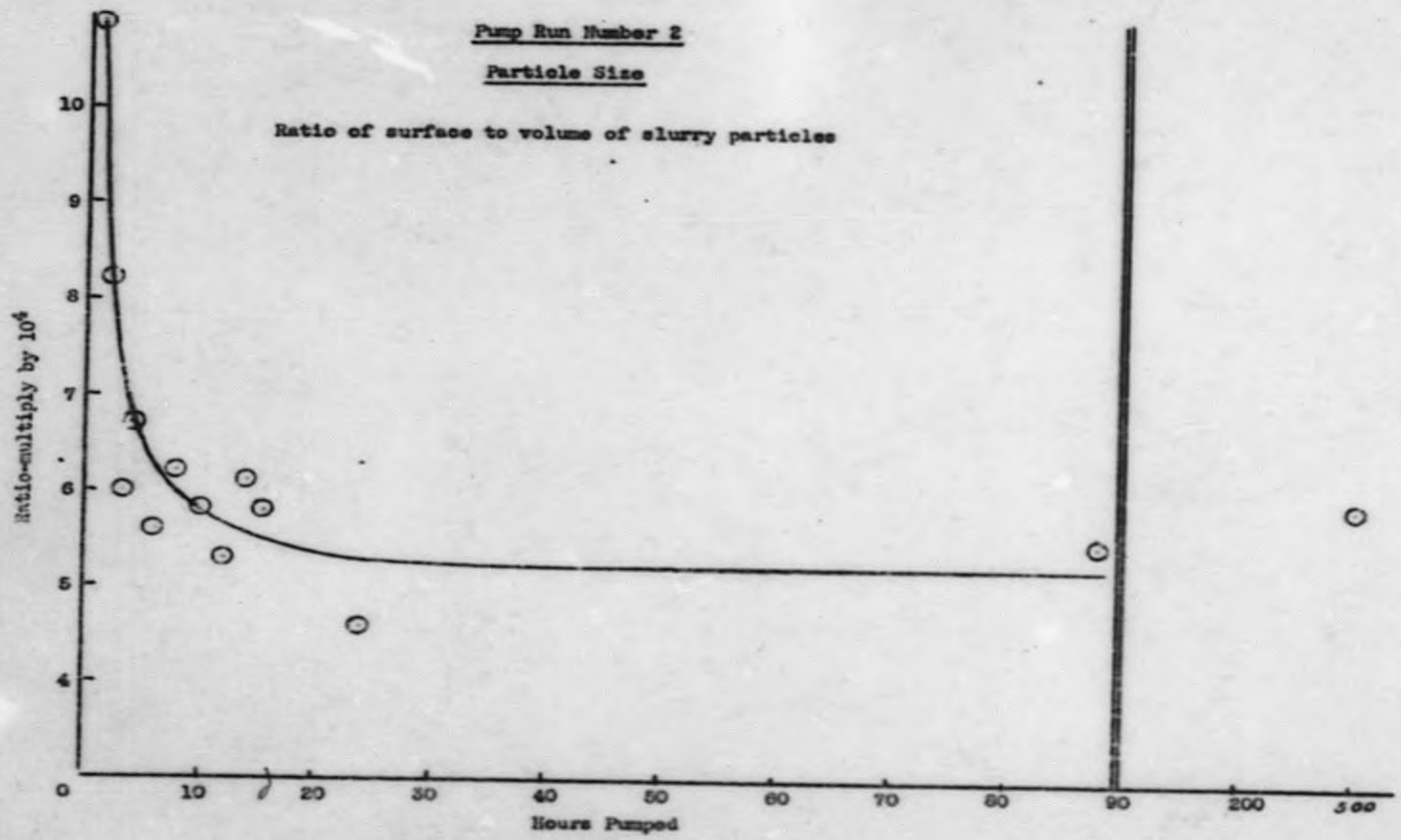
There remains the question of what index of particle size is most indicative of the state of the slurry. An estimate of the average surface to volume ratio seems a reasonably sound index inasmuch as the properties of viscosity and massive settling certainly must be affected by surface forces. In the tables below the samples have been given two designations. The SUC series refers to the number of the sample sent to Dr. Copeland for electron micrography.

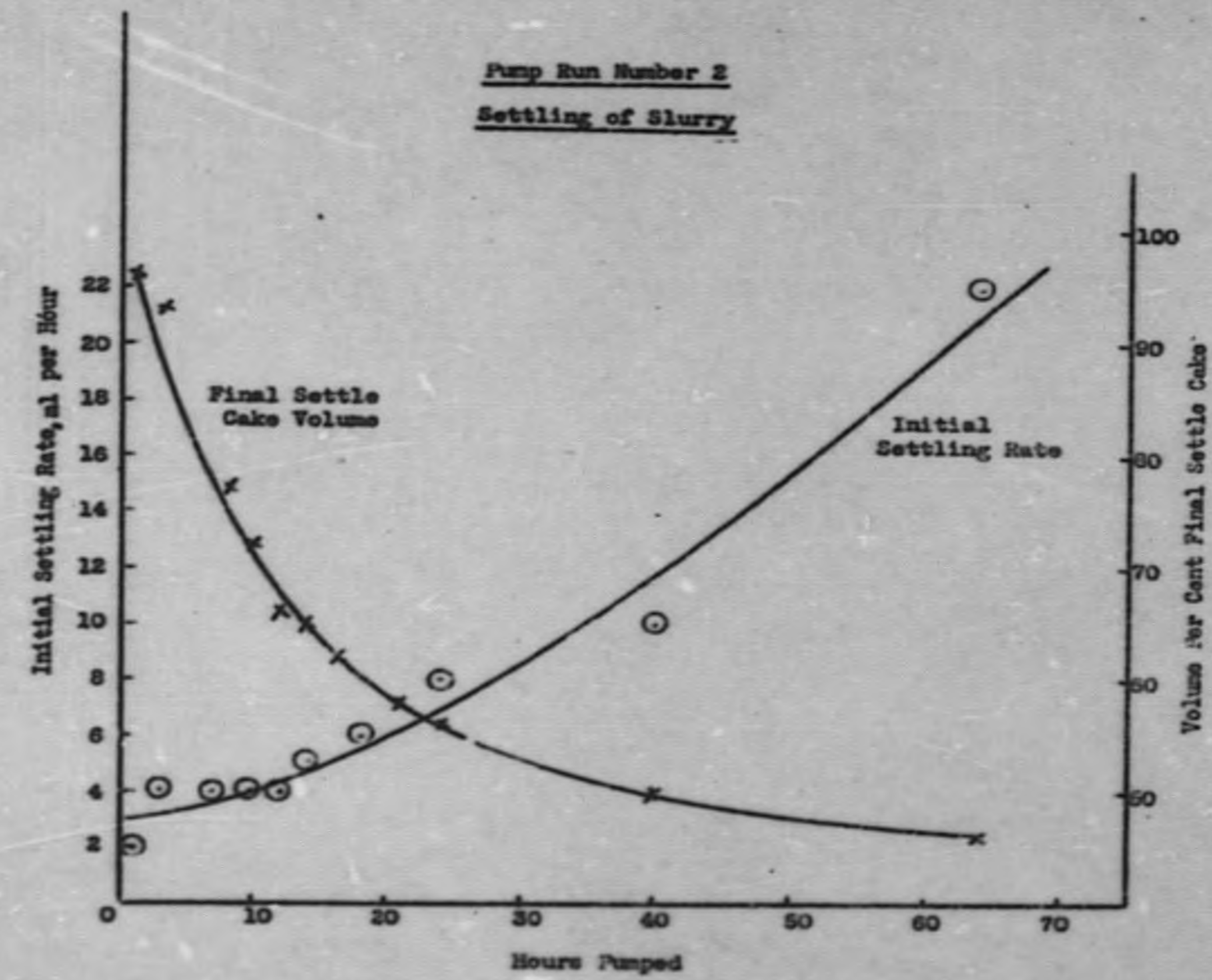
Pumping Run No. 2

Sample No.	MUC No.	Time of Pumping Hrs	Viscosity	Initial Settling Rate ml/hr	Ultimate Settling Volume-%	Particle size surface/volume cm^{-1}
1	40	1	177	2	96	10.9×10^4
2	42	2	155	---	--	8.2 "
3	44	3	155	4	93	6.0 "
4	46	4	142	----	--	6.7 "
5	48	6	111	----	--	5.6 "
6	50	8	96	4	77	6.2 "
7	52	10	89	4	72	5.8 "
8	54	12	78	4	66	5.3 "
9	56	14	67	5	65	6.1 "
10	58	16	64	6	62	5.8 "
11	---	21	62	7	58	----
12	62-63	24	59	8	56	4.6 "
13	---	40	57	10	50	----
14	---	64	51	22	46	----
15	69	88	52	---	---	5.5 "
16	---	208	---	---	---	----
17	---	256	44	---	---	----
18	---	280	40	---	---	----
19	85	304	44	---	---	5.9 "

Pumping Run No. 3

Sample No.	Time of Pumping Hrs	Viscosity	Ultimate Settling Volume-%
10	1.25	168	96
13	2	150	95
16	4	125	83
20	8	105	81
22	20	52	38
24	36	45	29


Pump Run Number 2
Particle Size
Ratio of surface to volume of slurry particles
Ratio-multiply by 10⁴
10
9
8
7
6
5
4
0
10
20
30
40
50
60
70
80
90
200
500
Hours Pumped


Pump Run Number 2
Settling of Slurry
Initial Settling Rate, ml per Hour
Volume Per Cent Final Settle Cake
Final Settle
Cake Volume
Initial
Settling Rate
Hours Pumped
0
10
20
30
40
50
60
70
2
4
6
8
10
12
14
16
18
20
22
50
60
70
80
90
100

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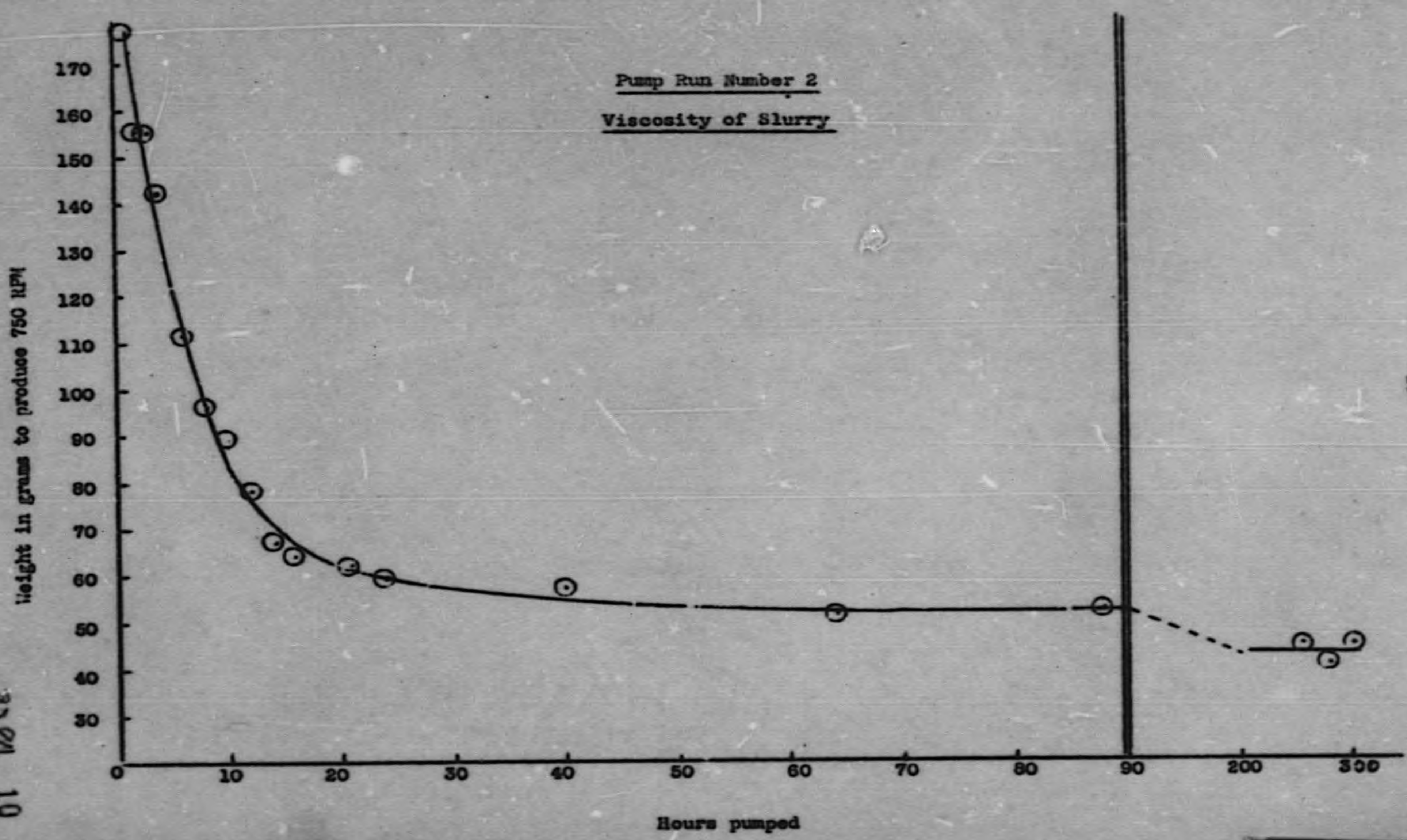
Pump Run Number 2
Viscosity of Slurry
Weight in grams to produce 750 RPM
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
0
10
20
30
40
50
60
70
80
90
200
300
Hours pumped