THE INFLUENCE OF THE PROXIMITY OF A SOLID WALL ON THE CONSISTENCY OF VISCOUS AND PLASTIC MATERIALS. IV

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INTRODUCTION

In the first paper (7) of this series experiments were described in which aqueous pastes of soils, clays, and finely divided minerals were forced through narrow glass tubes. The instrument used was the modified Bingham plastometer described in an earlier paper (13), in which two bulbs are connected by a tube of known length L and radius R. The material can be made to flow in either direction under a measured air pressure P. The volume V of flow per second was measured indirectly by the small back-pressure set up by the air in escaping through one of a series of standardized capillary leaks.

The data so obtained presented a problem, for on plotting $V/\pi R^3$ against $PR/2L$ ($= W$, the shearing stress per unit area on the wall of the tube) the points for tubes of different radii did not fall on the same curve, those for a narrower tube lying above those for a wider one. It was already known from the work of Bingham (2) and others, that such materials do not conform to Poiseuille's law, which means that the velocity gradient is not directly proportional to the shearing stress as it is for true fluids; but it was shown that no equation of dependence of velocity gradient on shearing stress, however complicated, would account for the phenomenon. The discrepancy is far too large to be put down to experimental error, and the only possible conclusion is that somewhere in the tube the velocity gradient depends on *something else besides the shearing stress.* So much seems certain.

An examination of the data obtained with a series of different radii led us to put forward the hypothesis that the *proximity of a solid wall* is the disturbing factor. It was suggested that, where the $V/\pi R^3$–W curves for different radii were not coincident, a shearing stress operating near the wall of the tube gives rise to a greater velocity gradient than does the same stress operating in the bulk of the material. In the subsequent papers of this series (8, 10) it was shown that although the data are not sufficiently exact to enable a precise estimate to be made of the thickness of the modified layer, in the case of a certain soil paste, it could not be greater than 8×10^{-3} cm. or less than 1×10^{-3} cm.

A different hypothesis has recently been put forward by Ambrose and Loomis (1) to account for the anomalous behavior of bentonite pastes. They point out that bentonite is known to be thixotropic, and suggest that the velocity gradient depends not only on the magnitude of the shearing stress, but also on the time it is applied. They conclude that this material appears to have a lower consistency the narrower the tube used, because "for constant shearing stress at the wall, the material flows at higher linear velocity in the larger tubes, thus being subjected to the same distribution of shearing stresses for a shorter time than in the smaller tubes."

While it is possible that, with the material used by these authors and under the conditions of their experiments, thixotropy may have been of importance, we do not think it can have had any measurable influence on our published data. Before any measurements were made, the whole of the material was driven through the tube from one bulb into the other, and although the direction of flow had to be reversed several times to get a complete set of points for a curve, the experimental figures give no indication that time of shear influences the rate of flow.[1] Feeling, nevertheless, that the matter should be further investigated, we have made new measurements on several of the materials studied before, using tubes which differ considerably in length as well as in radius. It is clear that, if the material flows more readily under a given stress the longer it is applied, the rate of extrusion under a given pressure gradient will increase with the length of a tube of given radius. Comparatively little work has been done on the effect of length of tube on consistency. Our own earlier experiments (13) were confined to a comparatively small difference of length. Ambrose and Loomis (1) quote Peek and Erickson (5) as having "learned that the apparent viscosity of agar solutions and starch pastes at constant shearing stress is lower in the longer tubes," though these authors themselves say that they "do not consider the data conclusive evidence of a difference of the type observed." On the contrary Staudinger and Heuer (17) state that "the solution of a high polymer (polystyrol) flowing through a long tube appears more viscous than in a short tube of the same diameter, since here, owing to the long fiber molecules, the hindrance to a normal flow is more marked" (our translation).

The point which we have set out to settle is, therefore, this: Is the variation of $V/\pi R^3$ for a given value of W, which we have observed in aqueous pastes of certain soils, clays, and minerals, directly associated with the

[1] When materials showing marked thixotropy are investigated in our instrument, the flowmeter readings for a given pressure do not remain steady, but tend to increase so long as the shearing is continued. In consequence of this, we have not published any data for such materials.

radius of the tube, or is the association indirect, the governing factor being in reality the proportions of the tube, i.e. the ratio of some function of the radius to the length?

GENERAL BEHAVIOR OF THE MATERIALS INVESTIGATED

Before giving detailed consideration to the new data, it will be as well to recapitulate very briefly the flow characteristics of the aqueous paste, which are fully set out in the paper already referred to. Four stages may be distinguished as the pressure gradient is increased from zero.

Stage I. No movement.

Stage II.[2] Slow movement as a solid plug, flow increasing linearly with pressure.

Stage III. A very rapid increase of flow with pressure, the plug being separated from the wall by a sheath of material in laminar flow.

Stage IV. Rapid flow increasing almost linearly with pressure, the central plug occupying only a small part of the cross section and having little influence.

According to the mathematical treatments of Buckingham (3) and Reiner (6) stage III is reached when the shearing stress W at the wall of the tube surpasses the critical shearing stress (S_0) of the material, and the sheath of material in laminar flow should have a thickness $R(W - S_0)/W$ which is proportional to the radius of the tube. The mean velocity of flow $V/\pi R^2$ for a given value of W greater than S_0 should therefore be proportional to R, which is another way of saying that the curve of $V/\pi R^3$ against W should be independent of R. The fact that the $V/\pi R^3$–W curve is not independent of R is interpreted by us as indicating that mean velocity of $V/\pi R^2$ may be resolved into two parts, one proportional to R, and the other independent of it. The part that is independent of R is mathematically similar to the term introduced by Buckingham to cover stage II. But whereas the velocity of sliding of the plug in stage II is so low that the lubricating sheath, assumed to consist of water, has a mean thickness of only 10^{-5} cm., the additional term needed to account for the flow in stages III and IV is about one hundred times as great.

In order to get a quantitative measure of the anomaly in stage IV, it was found convenient to plot the mean velocity $V/\pi R^2$ against W. The best straight lines making a common intercept on the W-axis were drawn, and their slopes σ plotted against R. The extent of the anomaly is indicated by the intercept σ_0 of this derived graph on the σ-axis; hence the name σ-phenomenon.

The need for a reiteration of the distinction between the "plug flow" of stage II and the anomalous flow near the wall of the tube which sometimes occurs in stages III and IV, is evident from a paper by Lawrence (4), who

[2] For work on stage II, see references 11, 12, and 16.

quotes our work and suggests that ammonium oleate sols show a "plug flow." This is demonstrably not so in the sense in which we use the words, and in any case it seems more likely that the disturbance he observes is due to the elasticity of the sol than to anomalous flow.

EXPERIMENTAL PART

As already recorded, the phenomenon under consideration was first observed in pastes of soils and clays. The composition of these materials is, however, highly variable, and the extent of the phenomenon depends on factors not all of which are understood. Since the question at issue is a fundamental one, it seemed wisest to use, for the present tests, a material of simple and known composition which is easily procurable by others who may wish to repeat the experiments. Barium sulfate (pure) as supplied by British Drug Houses was therefore selected. Microscopic examination showed that the material was reasonably homogeneous and consisted mainly of cubes with sides 2 to 3μ in length.

TABLE 1

(a)			(b)		
TUBE NO.	R	L	TUBE NO.	R	L
	cm.	*cm.*		*cm.*	*cm.*
h	0.131	4.7	III	0.073	12.10
j	0.126	7.5	IV	0.048	12.25
a	0.126	11.8	V	0.0407	12.30
b	0.129	22.5			

In preparing this paste, the barium sulfate was triturated with distilled water with a rubber pestle, then gently pressed through a 100 mesh per inch sieve, thoroughly stirred, sieved again, bottled, brought to temperature (25°C.) in the thermostat, well shaken and then tested in the plastometer (A). Another portion of the same sample was kept overnight, and tested the next day (B). The concentration of the two samples differed slightly, but a moisture test at the end of the second experiment showed that 100 g. of paste had contained about 55 g. of dry barium sulfate.

Owing to the tendency for the barium sulfate paste not to leave a clean surface on the walls of the plastometer tubes, the insides of the bulbs were coated with a thin layer of vaseline. This worked excellently until the material had been sheared a considerable number of times, when small spots of the vaseline surface rubbed off, and got into the capillary, readings then becoming erratic. This happening was well defined, all readings up to a certain time being steady and reproducible, but this difficulty precluded a comparison of a very great number of tubes in a single experiment.

Preliminary measurements made without the use of vaseline gave essentially similar results, but the accuracy was less, owing to the difficulty of observing the level of the material in the bulbs.

Moreover, slight losses of material during the changing of the tubes and the advisability of continuing a given experiment over too long a period of time also precluded the use of a very great number of tubes for each experiment, and introduced an element of haste into the experiments which prevented their accuracy from equalling that of the earlier and more leisurely experiments. They were, nevertheless, amply accurate for the purpose in hand.

TABLE 2

Results of experiment A

Capillaries are given in the order in which the experiments were done

CAPILLARY	RESISTANCE USED IN FLOWMETER	P_m	a	V	P	$W/100$	$V/100\,\pi R^3$
a	(2)	7.0	0.6	0.167	5.2	3.65	0.266
		8.0	1.2	0.333	6.15	4.35	0.535
		9.0	2.2	0.61	7.0	4.94	0.985
		10.0	4.1	1.14	7.8	5.50	1.84
		11.0	7.1	1.97	8.6	6.05	3.18
		12.0	9.1 (?)	2.52 (?)	9.5	6.70	4.07 (?)
b	(2)	13.0	2.0	0.555	11.0	4.17	0.825
		15.0	3.1	0.86	12.9	4.90	1.28
		17.0	5.5	1.53	14.85	5.65	2.27
		19.0	9.0	2.50	16.5	6.25	3.72
		21.0	14.0 (?)	3.90 (?)	18.3	6.95	5.80 (?)
j	(2)	5.0	0.6	0.167	3.2	3.59	0.265
		6.0	1.4	0.388	4.1	4.6	0.619
		7.0	3.9	1.08	4.85	5.45	1.71
		8.0	6.9	1.91	5.6	6.3	3.02
		9.0	10.5	2.90	6.4	7.2	4.60
V	(6)	10.0	0.3	0.009	8.4	1.85	0.425
		12.0	0.6	0.017	10.4	2.28	0.800
		14.0	1.0	0.029	12.4	2.72	1.38
		16.0	1.3	0.038	14.4	3.17	1.80
		18.0	1.8	0.052	16.3	3.59	2.45
		20.0	2.3	0.067	18.3	4.02	3.15

The plastometer bulbs were connected to the capillary by means of rubber sleeves. In earlier papers (14, 15) it was shown that such a procedure was liable to cause unexpected errors in the case of saturated solutions of very soluble salts, but that no such errors occur in the case of pastes of soils or clays. There is no reason to suspect any such trouble with pastes of insoluble barium sulfate, and in any case the effect would be small compared with the very gross phenomena being investigated in these experiments. A series of tubes having the dimensions shown in table 1(a), was prepared. The radii were determined by a viscometric comparison with our previously carefully standardized tubes (table 1(b)) by measuring the

TABLE 3

Results of experiment B

CAPILLARY	RESISTANCE USED IN FLOWMETER	P_m	a	V	P	$W/100$	$V/100\ \pi R^3$
V	(6)	8.0	0.2	0.006	6.5	1.43	0.280
		12.0	0.4	0.012	10.5	2.30	0.569
		16.0	0.8	0.023	14.5	3.18	1.09
		20.0	1.5	0.044	18.5	4.07	2.07
		22.0	2.0	0.058	20.4	4.50	2.75
		24.0	2.7	0.078	22.4	4.92	3.70
		26.0	3.2	0.093	24.4	5.39	4.40
III	(6)	8.0	0.7	0.020	6.5	2.60	0.165
		10.0	1.5	0.044	8.5	3.40	0.365
		12.0	3.3	0.096	10.4	4.15	0.795
		14.0	5.6	0.162	12.2	4.88	1.34
		16.0	9.2	0.267	14.1	5.62	2.22
		18.0	13.8	0.400	16.0	6.40	3.30
IV	(6)	15.0	0.8	0.023	13.5	3.50	0.665
		17.0	1.4	0.041	15.3	4.03	1.19
		20.0	2.4	0.070	18.4	4.73	2.04
		22.0	3.5	0.102	20.3	5.25	2.95
		25.0	4.3	0.125	23.2	6.02	3.62
		27.0	5.2	0.151	25.2	6.55	4.38
a (incomplete)	(2)	8.0	1.0	0.277	6.15	4.33	0.448
		11.0	4.0	1.11	8.8	6.18	1.80

flow/stress ratio for a glycerol–water solution for each tube, and so calculating R. Corrections for resistance in plastometer bulbs were made throughout by connecting the bulbs directly together as described in the first paper of this series (7).

Tube h showed slightly anomalous behavior, but, since its L/R ratio is only 36, this was disregarded.

Since the presence of a small metal disk drilled with a hole of 0.14 cm. radius in place of a capillary made no serious difference to the plastometer resistance, end-effect corrections were neglected. (Cv. Ambrose and Loomis' criticisms of capillary tube methods.)

Table 2 gives the results of experiment A, and table 3 of experiment B. The data are also plotted in figures 1 and 2, plotting $V/100\pi R^3$ against $\frac{W}{100}$, where $W = PR\Delta g/2L$. V is flow in cubic centimeters per second and equals flowmeter reading "a" $\times$ appropriate constant. P is pressure (cm. Hg) corrected for bulb resistance, and P_m the uncorrected pressure as read on the manometer.

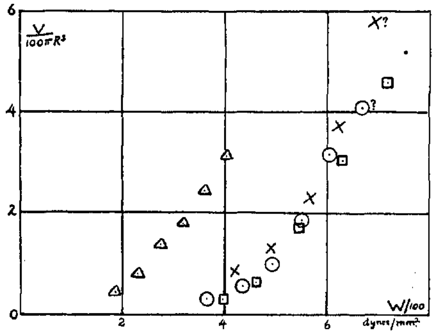

FIG. 1

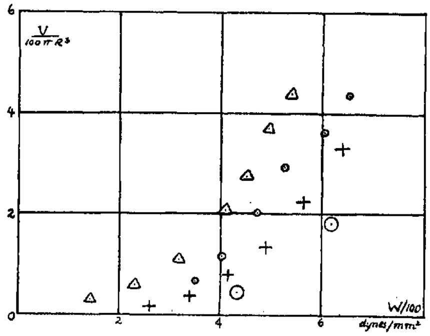

FIG. 2

FIG. 1

⊙ Capillary a, R = 0.126 cm., L = 11.8 cm.
△ Capillary V, R = 0.0407 cm., L = 12.3 cm.
× Capillary b, R = 0.129 cm., L = 22.5 cm.
⊡ Capillary j, R = 0.126 cm., L = 7.5 cm.

FIG. 2

⊙ Capillary a, R = 0.126 cm., L = 11.8 cm.
△ Capillary V, R = 0.0407 cm., L = 12.3 cm.
+ Capillary III, R = 0.073 cm., L = 12.1 cm.
⊙ Capillary IV, R = 0.048 cm., L = 12.25 cm.

The figures in the second column of each table refer to the resistance used in the flowmeter. For (2) flowmeter readings (a) are multiplied by 0.277. For (6) flowmeter readings (a) are multiplied by 0.029.

Figure 1 shows that length of tube has no effect on consistency, within the limits investigated, whereas the tube having a different radius shows an entirely different curve. The σ-effect (effect of radius) is shown more definitely in experiment B (figure 2).

The maximum length of tube used was 40 cm., as compared with 10 cm. in the earlier experiments, and with the apparatus in its present form stage IV could only be reached at the highest pressures. Most of the points therefore, are in stage III. This makes the data unsuitable for evaluating σ_0, but does not prevent their being used to decide whether an anomaly exists in connection with variations in length at constant radius.

Essentially similar results were obtained in some preliminary tests with soils, but for the reasons already stated, we have given the details of the experiments only in the case of barium sulfate.

CONCLUSIONS

These measurements show quite conclusively that for barium sulfate paste the rate of flow in tubes of a given radius and under a given pressure gradient (within the limits used) is independent of the length of the tube. The data thus lend no support to the idea that this material suffers a progressive breakdown with time under shear.

The effect of changing the radius upon the position of the $V/\pi R^3$–$PR/2L$ curves is as marked as in the earlier experiments on this material. From a calculation made from the curves published in an earlier paper (7), it may be concluded that the thickness of the layer which is modified by its proximity to the wall of the tube cannot be less than 20μ (the thickness, if this layer had the viscosity of pure water). This is very remarkable, since we now know that the individual particles are only 2 to 3μ in linear diameter. The thickness of the modified layer seems to be more comparable with the size of the flocculated aggregates as shown by sedimentation.

SUMMARY

Measurements have been made of the rate of flow of an aqueous paste of barium sulfate through tubes differing considerably both in radius and length under a series of pressure heads. The results show that for tubes of the same radius and under the same pressure gradient, the rate of flow is independent of the length of the tube; from which it is concluded that under the conditions of these experiments, this material shows no progressive breakdown with time under shear, as suggested by Ambrose and Loomis (1) for bentonite.

For different radii, however, curves for $V/\pi R^3$ against $PR/2L$ were obtained which, as previously recorded, do not coincide as they should if at every point in the tube the velocity gradient depends only on the shearing stress.

The hypothesis previously advanced that the proximity of the wall of the tube causes a sheath of material to shear more easily than does the bulk of the material, appears therefore to be the only one so far advanced that accounts for the facts.

The case of this barium sulfate paste is particularly interesting, as the particles are roughly cubical in form, and the thickness of the modified layer is many times the average particle diameter.

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