W2

Reprinted from Transactions of the Indian Ceramic Society, Vol. 41 (2) March-April 1982

Rheological Properties of Clay Pastes—Part II: Thixotropic Co-efficient at Liquid Limit Consistency

R. B. HAJELA AND J. M. BHATNAGAR

Central Building Research Institute
Roorkee-247 667 (UP)

Studies on the application of rheological properties of clay pastes from red, black and alluvial clays for the determination of liquid limit have been further extended to determine the thixotropic co-efficient of various clays at liquid limit consistency. The thixotropic co-efficient at liquid limit consistency, irrespective of clay mineral composition varies in a narrow range of 0.7 to 1.50. At this consistency, the Bingham yield stress and thixotropic area also vary in a narrow range. The plot between thixotropic co-efficient and moisture content at liquid limit of various clays holds two linear relationships: (i) for plastic clays having liquid limit above 50 and (ii) for lean clays having liquid limit below 50±2. The small variations occurring in thixotropic co-efficient at liquid limit consistency have been attributed to the nature of exchangeable and adsorbed ions, organic matter, non-clay fractions, surface roughness on sand and silt particles etc.

Introduction

In earlier publications[1,2] a rheological method for the determination of liquid limit of various alluvial, black and red soils of India has been reported. The method is based on (a) the extrapolation of Bingham yield stress from the hysteresis curve of clay paste and (b) thixotropic break-down of clay water system at various moistures close to liquid limit consistency and when plotted against moisture content yield two linear curves. The point of intersection of these curves corresponds to Bingham yield stress/thixotropic break-down of clay paste at liquid limit consistency of the clays. The thixotropic break-down and Bingham yield stress of various clays, irrespective of its clay mineral composition, at liquid limit consistency vary in a narrow range of 3.4 to 4.6 sq cm and 16 to 32 gm/cm² respectively. This observation corroborates the contention of Terzaghi,[3] Casagrande,[4] and Norman[5] that cohesive clays at the boundary of liquid and plastic behaviour should exhibit a small threshold shearing strength. This study has been further extended to determine the variation of thixotropic co-efficient of clay paste at various moistures close to liquid limit consistency. The results of correlation between thixotropic co-efficient and Bingham yield stress of clays at liquid limit consistency, thixotropic breakdown and activity co-efficient are reported in this paper.

Experimental

Alluvial, black, red and marine clays of India, having different mineralogical compositions, were selected for this study. All these clays were processed as specified in ASTM[6] designation 0423-66, 1966. The physical properties,[1,2] organic matter, soluble salts,[7-10] clay and non-clay minerals associated with the soils as identified by X-ray, thermal analysis, microscopic and megascopic examination, adopting standard procedures[7-10] are given in Table I as also in earlier publications.

The clay pastes at various moistures, close to liquid limit consistency, were prepared. The apparent viscosity of clay pastes at various moistures and at shearing rates varying from 0.5 to 100 rpm using Brookfield Synchrolectic viscometer[1] (RVT) with spindle No. 7 and at a temperature of 27±2°C was determined. The procedure involved the measurement of torque in the spring when the spindle of the viscometer is rotated at several constant rpm as has been reported[1,2] earlier. The apparent viscosity has been calculated from the equation

$$\eta_{\text{app}} = K \times \frac{\text{shear stress } (F)}{\text{rate of shear } (S)}$$

where K is instrumental constant.

Measurement of Thixotropic Co-efficient

Bingham[11] postulated that the rate of shear of a true plastic body is directly proportional to the shearing stress in excess of the yield value. Based on this concept, Bingham deduced a rheological equation

$$\eta_{\text{app}} = \eta_{\text{abs}} + \theta/S$$

which holds good for non-Newtonian fluid systems, where

η_{app} = apparent viscosity at shear rates,
η_{abs} = absolute viscosity, and
θ = co-efficient of thixotropy.

At high rates of shear, η_{app} approaches η_{abs}. This is reasonable, since at high shear rates thixotropic breakdown will occur. Goodeve and Whitfield[12] have applied this equation to clay slips and have obtained the values of thixotropic co-efficient θ by plotting apparent Viscosity η_{app} against reciprocal of rate of shear $1/S$. These plots should in fact yield a straight line of slope θ if Bingham equation holds good. The results of Goodeve and Whitfield[12] gave curve; the straight portion on extrapolation gave the values of intercept η_{abs} and tangent of the curve gave thixotropic co-efficient θ.

It has been reported by Moore and Davies[13] that Bingham equation does not hold good at low rates of shear (i.e. θ is not constant) and has emphasised the importance of time factor indicating the build-up of viscosity or regain of strength in structure. Worrall and Ryan[14] have adopted the aforesaid procedure of Goodeve and Whitfield[12] to compute the values of thixotropic co-efficient (θ) and absolute viscosity (η_{abs}) of monoionic clay suspension in the presence of electrolytes. They have obtained a straight line indicating, over the range of shear used, that thixotropic co-efficient is constant and the Bingham equation is held valid.

Results and Discussion

The plots between apparent viscosity at various reciprocal rates of shear for three soils, namely, black soil from Morbi (Gujarat), alluvial clay from Dimapur (Naga Land) and red soil from Cheranmaha Devi (Tamil Nadu) are given in Fig. 1, a, b & c. The curves are linear at higher rates of shear, which however show deviation from linearity at lower rates of shear, particularly in pastes containing moisture slightly below liquid limit consistency. A similar observation has also been reported by Goodeve and Whitfield,[12] Moore and Davies[13] as discussed earlier.

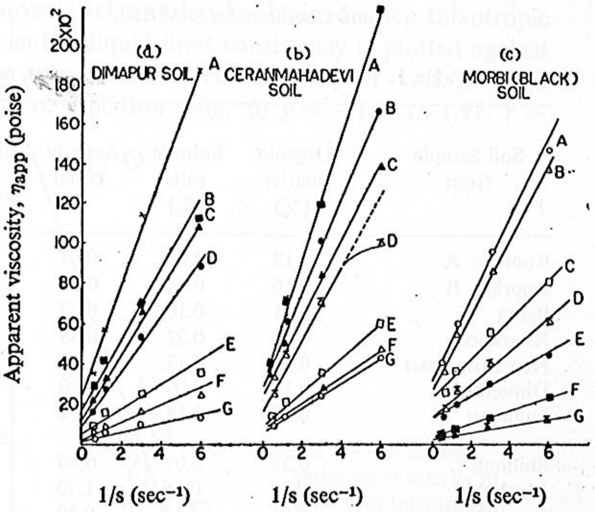

Fig. 1—Plot between apparent viscosity and reciprocal shear rate at varying moisture contents of different soils. (a) Dimapur, (b) Cheranmaha Devi and (c) Morbi (black).

The thixotropic co-efficient of clay paste at various moisture contents from the linear portion of the curve was extrapolated and the values so obtained are given in Table I. On plotting thixotropic co-efficient θ against moisture content two linear curves are obtained. The point of intersection of these curves correspond to liquid limit and thixotropic co-efficient at liquid limit consistency (Fig. 2). At this point, the behaviour of clay water mass just tends to change from liquid state to plastic state,[15] and the clay mass may show an optimum thixotropic behaviour and a critically small threshold stress. The thixotropic co-efficient at liquid limit consistency for 20 different clays, containing different clay mineral composition, has been found to vary in small range of 0.70 to 1.50 (Table I). It has been reported[1,2] earlier that thixotropic break-down and Bingham yield stress at liquid limit consistency vary in a narrow range of 3.4 to 4.6 sq cm and 16 to 32 gm/cm² respectively. Further, the liquid limit determined by thixotropic co-efficient method (Fig. 2) for 20 soils is comparable with the values obtained by Casagrande's method,[4] holding a linear relationship which follows a regression equation (Fig. 3), $y = x + 0.3$ and co-rrelation co-efficient $r = 0.99$ for 20 dof with probability factor[16] $p = 0.001$.

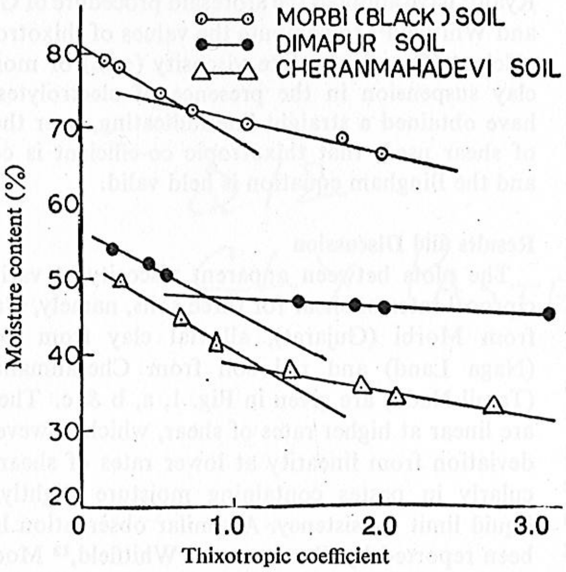

Fig. 2—Plot showing variation of thixotropic coefficient and moisture content of Morbi (black), Dimapur and Cheranmaha Devi Soil.

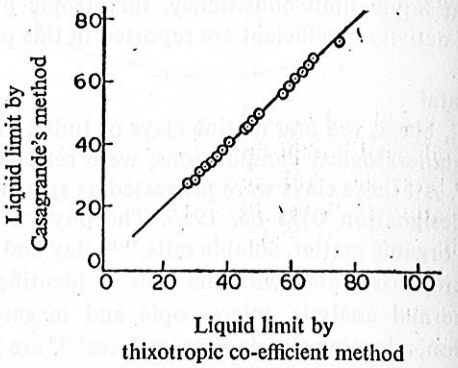

Fig. 3—Plot between liquid limit obtained by Casagrande's method and thixotropic co-efficient method.

It may be observed that the plots between thixotropic co-efficient on x-axis and moisture content at liquid limit consistency of various clays on y-axis (Fig. 4) hold two linear curves with regression equation (i) $y = -24.76x + 86.30$ for plastic clays possessing liquid limit values above 50±2, $r = -0.95$ for 8 dof and

Table I: Results of organic matter, soluble salts, activity and thixotropic co-efficient and minerals present in various soils

Soil Sample from	Organic matter (%)	Soluble salts (%)	Activity co-eff	Thixotropic co-eff	Minerals present Predominant	Minerals present Accessory
Roorkee A	0.12	0.09	0.65	1.06	illite, kaolinite	quartz, attapulgite
Roorkee B	0.16	0.14	0.70	0.90	illite, kaolinite	quartz, vermiculite, goethite
Patna	0.21	0.10	0.62	1.05	illite, kaolinite (disordered)	quartz, hematite, goethite
Kharkhoda	0.06	0.22	0.55	1.05	illite, kaolinite	biotite, calcite
New Missamari	0.23	0.12	1.70	0.85	muscovite, kaolinite	vermiculite, quartz, chlorite
Dimapur 'A'	0.17	0.09	0.90	0.85	illite, muscovite, kaolinite	hematite, biotite, quartz, magnetite
Dimapur 'B'	0.26	0.14	0.82	0.90	halloysite/kaolinite (disordered), illite	goethite, zircon, orthoclase, magnetite
Shillong.	0.32	0.07	0.86	0.85	montmorillonite, illite	hematite, quartz, garnet, corundum
Morbi 'A'	0.49	0.16	1.70	0.70	montmorillonite, kaolinite	quartz, calcite, zircon
Pondicherry	0.06	0.12	0.89	1.05	kaolinite, montmorillonite	quartz, calcite, attapulgite
Madras	0.32	0.14	0.86	0.90	montmorillonite, illite; kaolinite	biotite, calcite, hematite
Indore	0.43	0.12	0.55	1.00	montmorillonite, kaolinite	quartz, goethite, dolomite
Gulbarga	0.37	0.16	1.00	0.70	montmorillonite, kaolinite	quartz, dolomite, microcline,
Quilon	2.17	0.18	0.85	1.20	kaolinite	goethite, gibbsite
Cheranmaha Devi	0.15	0.12	0.50	0.95	kaolinite (disordered), illite	hematite, quartz, chert
Manmadurai	0.36	0.16	0.60	1.50	kaolinite (disordered), muscovite	quartz, hematite, augite
Bangalore	0.31	0.10	0.40	0.95	kaolinite	quartz, hematite, olivine
Jhansi	0.23	0.08	0.44	0.95	beidellite, kaolinite, montmorillonite	quartz, hematite, goethite, orthoclase, dolomite
Morbi 'B'	0.14	0.12	0.74	1.00	kaolinite	hematite, quartz, calcite, iron oxide,
Kandla	1.26	4.31	1.10	0.90	illite, glauconite, halloysite	quartz, carbonates, augite, attapulgite

(ii) $y = -34.42x + 70.2$ for lean clays possessing liquid limit below 50 ± 2; $r = -0.40$ for 12 dof. The co-efficient of co-rrelation for clays having liquid limit below 50 ± 2 under equation (ii) is low as the probability factor (p) for co-rrelation is above 0.10. This could be attributed to the particle size effect, presence of large proportions of extraneous non-plastic matter in the soil, poor cohesion between particles etc which largely modify the thixotropic properties and flow behaviour of clay mass[17,18] at this consistency.

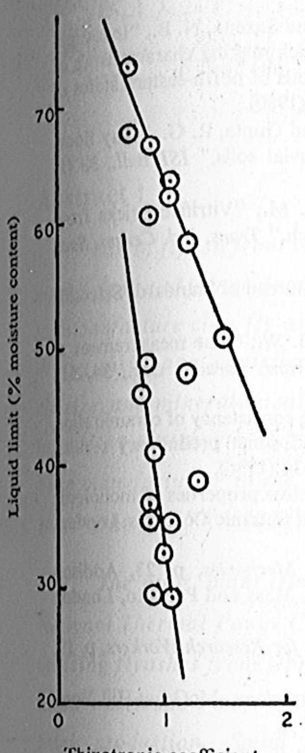

Fig. 4—Plot showing variation of liquid limit with thixotropic co-efficient (at liquid limit consistency).

The plot between thixotropic co-efficient or magnitude of thixotropic break-down (abscissa) and Bingham yield stress (ordinate) for various soils at liquid limit consistency (Fig. 5, A & B), shows ill-defined linearity, as in a narrow range Bingham yield stress is largely modified. This indicates the order of rigidity with which few outer most molecular layers of water contributing to the slippage or lubricating property, are adhering over the well oriented net-work of clay-water skeletal structures[19-21] at liquid limit consistency. This rigidity is expected to increase with the increase in cohesion between particles and thixotropic behaviour of the clay mass (Fig. 5, A & B). Rosenquist,[19] Houwink,[22] Anderson and Low,[23] and Low[24] have reported that the water within the few molecular layers of clay mineral surfaces has different properties than the water in the bulk. The manner in which the properties of the near surface water differ, from those of normal water, remains unresolved. In clay-water system there is likely to be a range in the forces of interparticle attraction, due to differences in bond type, so that the energy barrier to motion between the particles will vary. Application of the force, insufficient to cause rupture, may cause yielding of the weaker bonds and/or slippage in the few outer most layers of water adhering over the net-work of gel structure.

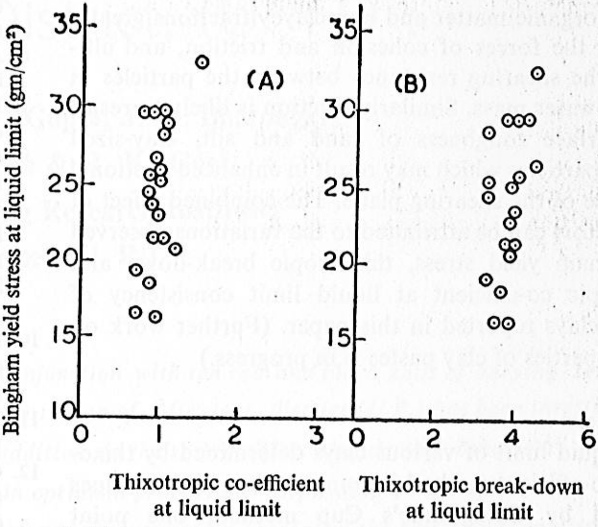

Fig. 5—Plots showing variation between Bingham yield stress and thixotropic co-efficient (A) and thixotropic break-down (B) at liquid limit.

An inverse relationship is obtained when thixotropic co-efficient at liquid limit consistency is plotted against activity (plastic index/clay content) of various clays holding an equation (Fig. 6) $y = -1.15x + 1.97$, $r = -0.49$ for 20 dof and probability factor $p = 0.02$ to 0.05. This shows that clays of high activity possess low thixotropic co-efficient at liquid limit consistency.

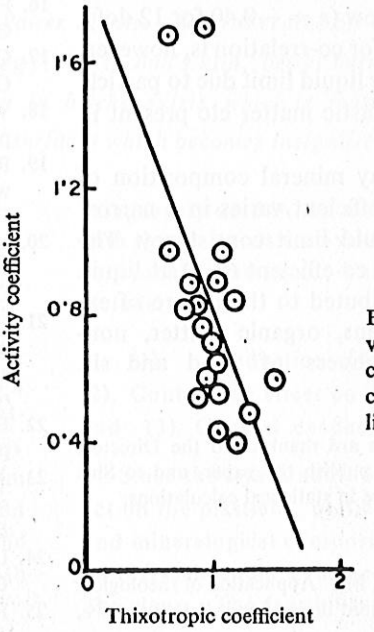

Fig 6—Plot showing variation of activity of clays with thixotropic coefficient at liquid limit consistency.

It is well-known that thixotropic property of clay-water mass involves a combination of attractive forces between the particles[18] and the lubricating action of a liquid between the particles,[19] the shape and size of the particles, the distance of their separation, the strength of attractive forces and the physical state[20-25] of the liquid. The nature of exchangeable cations, absorbed cations, organic matter and non-clayey fractions greatly modifies the forces of cohesion and friction, and ultimately the shearing resistance between the particles in the clay-water mass. Similarly, friction is likely to result from surface roughness of sand and silt, clay-sized mineral particles which may result in enhanced frictional resistance of the shearing plane. The combined effect of these factors can be attributed to the variations observed in Bingham yield stress, thixotropic break-down and thixotropic co-efficient at liquid limit consistency of various clays reported in this paper. (Further work on flow properties of clay pastes is in progress.)

Conclusions

(i) Liquid limit of various clays determined by thixotropic co-efficient method is comparable with the values obtained by Casagrande's Cup method, one point method and rheological method.

(ii) The plots between thixotropic co-efficient and moisture content at liquid consistency hold two linear relationships:

(a) for plastic clays, having liquid limit above 50 ± 2;

(b) for lean clays, having liquid limit below 50 ± 2. The co-efficient of co-rrelation (r) for plastic clays under (a) is high ($r = -0.95$ for 8 dof) and for lean clays under (b) is low ($r = -0.40$ for 12 dof).

The probability factor (p) for co-rrelation is, however, above 0.1 for clays having low liquid limit due to particle size effect, extraneous non-plastic matter etc present in the clays.

(iii) Irrespective of the clay mineral composition of the soils, the thixotropic co-efficient varies in a narrow range of 0.70 to 1.50 at liquid limit consistency. The variations in the thixotropic co-efficient (θ_{LL}) at liquid limit consistency can be attributed to the nature of exchangeable and adsorbed ions, organic matter, non-clay fraction, surface roughness of sand and silt particles etc.

Acknowledgements: The authors are thankful to the Director, CBRI for his kind permission to publish the paper, and to Shri Sharafat Ali, Scientist for assistance in statistical calculations.

References

1. Hajela, R. B. and Bhatnagar, J. M., "Application of rheological measurements to determine liquid limit of soils," *Soil Science*, **114** (2) 122–30 (1972).
2. Hajela, R. B. and Bhatnagar, J. M., "Rheological properties of clay pastes—Part I: Thixotropy at liquid limit consistency," *Trans. Ind. Ceram. Soc.*, **41** (1) 10–13 (1982).
3. Terzaghi, K., "Erdbaumechanik auf boden physikalischer Grundlage," *Franz Deudicke*, Vienna (1925).
4. Casagrande, A., "Research on the Atterberg limits of soils," *Public Roads*, **13**, 121–30 (1932).
5. Norman, L. E. J., "A comparison of values of liquid limit determined with apparatus having bases of different hardness," *Geotechnique*, 2, 79–83 (1958).
6. ASTM procedure for testing soils, Standard method of test for liquid limit of soils, ASTM Desig. D: 423-66, 217–21 (1969).
7. Bhatnagar, J. M., Ph.D. Thesis, Dept of Chemistry, University of Roorkee, Roorkee (1978).
8. Hajela, R. B., Bhatnagar, J. M. and Saxena, N. B., "Investigations on physico-chemical and brick making characteristics of Brahmaputra alluvium and red soils of north-eastern states of India," *Ind. Ceram.*, **23** (1) 69–73 (1980).
9. Hajela, R. B., Bhatnagar, J. M. and Gupta, R. G., "Clay flooring and terracing tiles from alluvial soils," *ISI Bull.*, **33** (1) 12–17 (1981).
10. Hajela, R. B. and Bhatnagar, J. M., "Vitrified bricks from coastal alluvium of Rann of Kutch," *Trans. Ind. Ceram. Soc.*, **34** (3) 49–53 (1975).
11. Bingham, E. C., "Viscosity," US Bureau of Standards Scientific Paper No. 278 (1916).
12. Goodeve, C. F. and Whitfield, G. W., "The measurement of thixotropy in absolute units," *Trans. Faraday Soc.*, **34**, 511 (1938).
13. Moore, F. and Davies, L. J., "The consistency of ceramic slips, A new rotational viscometer and some preliminary results," *Trans. Brit. Ceram. Soc.*, **55**, 313–38 (1956).
14. Worrall, W. E. and Ryan, W., "Flow properties of monoionic clay suspensions, VII International Ceramic Congress, London, pp. 421–33 (1960).
15. Scott, R. F., *Principles of Soil Mechanics*, p. 23, Addison Wesley Publishing Co., Reading, Mass and Paloalto, London (1963).
16. Fisher, R. A., *Statistical Methods for Research Workers*, p. 19, Oliver and Boyd, London (1950).
17. Grim, R. E., *Applied Clay Mineralogy*, McGraw-Hill Book Co., New York (1962).
18. Van Olphen, H., *An Introduction to Clay Colloid Chemistry*, p. 301, John Wiley and Sons, New York (1963).
19. Rosenquist, I. Th., "Physico-chemical properties of soils: Soil water systems," Proc. Amer. Soc. Civil Engrs., J. Soil Mech. Found. Div., **85** (SM 2) 31–53 (1959).
20. Lambe, T. W., "A mechanistic picture of shear strength in clays," *Amer. Soc. Civil Engrs. Res. Conf. on Shear Strength Cohesive Soils*, Boulder Colo., pp. 555–80 (1960).
21. Warkentin, B. P. and Yong, R. N., "Shear Strength of montmorillonite and kaolinite related to interparticle forces, clays and clay minerals," *Proc. Natl. Conf. on Clays and Clay Minerals*, **9**, pp. 210–19 (1960).
22. Houwink, R., *Elasticity, Plasticity and the Structure of Matter*, p. 368, Harren Press, Washington D.C. (1953).
23. Anderson, D. M. and Low, P. F., "The density of Water adsorbed on Li, Na and K bentonite," *Soil Science Soc. Am. Proc.*, **22**, pp. 99–103 (1958).
24. Low, P. F., "Viscosity of water in clay systems," *Proc, Natl. Conf. on Clays and Clay Minerals*, **8**, pp. 170–82 (1959).
25. Martin, R. T., "Adsorbed water in clay: A review," *Proc. Natl. Conf. on Clays and Clay Minerals*, **9**, pp. 28–70 (1962).

[MS received January 8, 1981; revised copy received February, 14, 1982]