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Sedimentation tests for rolling oils

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Sedimentation experiments have been performed with steel and iron oxide micrometre-sized particles in pure liquids and industrial oils emulsified in water. They demonstrated the influence of viscosity and the action of certain surfactants dissolved in pure liquids on the aggregation or dispersion of the particles. It was also seen that some stable emulsions can be broken down by the presence of the particles which adsorb the surfactants from the emulsions. The results of these novel tests are positively correlated with the rolling oil quality in industrial conditions.

1. Introduction

The steel industry has recently received much pressure from the market to improve drastically its competitiveness and the quality of its production. The making of steel cold-rolled products "faster and cleaner" is a major challenge. In this respect the efficiency of a cold rolling mill is strongly dependent on the rolling oil: the better the oil, the larger plate reduction, and the cleaner is the steel strip surface [1, 2].

Rolling induces an unavoidable production of micrometre-sized steel particles which emanate mainly from the strip reduction and to a smaller extent from the rolls wear. When the rolling emulsion is recirculated, the presence of such particles in the filtered liquid, even in minute amounts, constitutes a real drawback for the standard quality of the final product: it affects both the steel surface state and the properties of the emulsion. The minimization of these amounts requires a better understanding of the interactions between the steel particles and the various constituents of the emulsion. In the gravity settlers of the mills, the steel particles should be able to settle or to float without excessive breakdown of the emulsion and oil consumption: this is related to the wettability properties of the solid particles by the liquids which are strongly dependent on their respective surface tensions [3].

Recently, wetting has been quite extensively studied for pure systems on well-defined plates or powders [4, 5]. Now, for our purpose, a major difficulty arises from the heterogeneity of the industrial materials in any respect, ore, mineral oils and fats of various origins, particles of various shape, size and chemical nature, surfactants, pressure additives of various compositions, and so on. The usual homologation tests do not provide any information on the previous concerns and it is the aim of this paper to fill in that gap.

A test on the sedimentation of steel particles in various liquids and rolling emulsions is convenient: it is quite simple and global enough for the system heterogeneities; in addition, it provides essential qualitative information on the interactions of various constituents [6]. Indeed, when solid particles are introduced in suspending liquids, there is a "new arrangement" of the constituents (surfactants adsorption, oil droplets coalescence, particle aggregation or dispersion, etc.) which definitely influences the rate and final volume of sedimentation and the aspect of the supernatant emulsion.

This paper presents results for non-emulsified liquids (pure laboratory ones and three industrial oils) which clearly display the influence of viscosity and the action of known surfactants dissolved in pure liquids on the possible aggregation or dispersion of the particles. Experiments were also carried out with oil-in-water emulsions, showing their difference with respect to particle aggregation and emulsion breakdown.

2. Experimental procedure

2.1. Materials

The sedimentation tests were performed in small Pyrex tubes (115 mm long, 6 mm i.d.).

2.1.1. *Powders*

Steel powder was obtained from the sludge accumulated on the magnetic filters of the rolling mill. The sludge was dissolved in trichloroethylene then filtered and washed twice in a Soxhlet extractor again with trichloroethylene for 2 or 3 days, then with acetone for another 2 days: after acetone evaporation the powder was kept under vacuum. Iron oxide powder (Fe_2O_3) was also systematically used in order to compare both types of behaviour. Scanning electron micrographs of these two powders are given in Fig. 1. The particles sizes are typically submicrometre.

2.1.2. *Liquids*

Various laboratory and industrial suspending liquids were used: alkanes and nitroethane (laboratory grade) saturated with pure water in which surfactants

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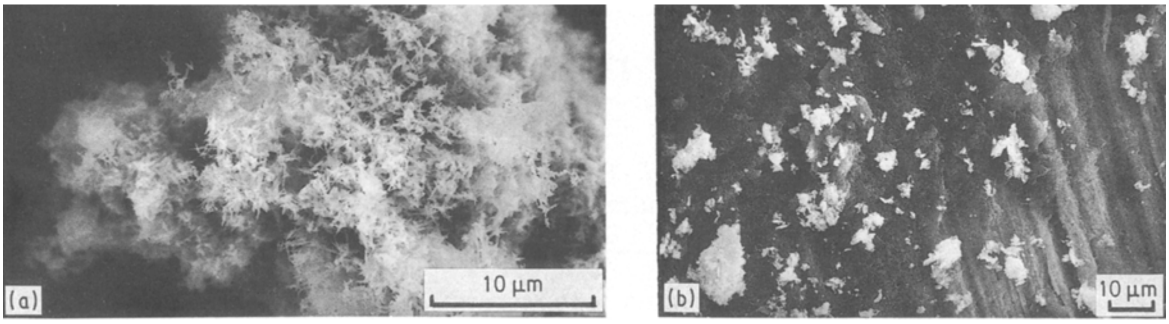

Figure 1 Scanning electron micrographs of the powders: (a) iron oxide, (b) steel.

were dissolved at different concentrations. Purified dodecyltrimethylammonium bromide (DTAB) and Tween 20 were used as surfactants. Three industrial oils from two companies named below, B, S, T, giving stable emulsions in water were also tested. Their compositions are unknown, but they are essentially apolar liquids (mixtures of mineral oils and fats) in which non-ionic surfactants among other additives have been dissolved. The physical properties of the liquids are summarized in Table I.

2.2. Procedure

An established procedure had to be rigorously followed to minimize reproducibility difficulties. Before use, glassware was carefully cleaned by removing fat with acetone and rinsing with water, bathing in fresh sulphochromic acid and rinsing with hot, then ultrapure, water, and finally drying at 120 °C.

The fluoroelastomer tube caps were cleaned with acetone in an ultrasonic bath (2 min) then in alcohol (2 min), and finally rinsed in water and dried at 60 °C.

Sterile single-use syringes with home-made stainless steel needles (120 mm long) with a 1 or 2 mm i.d.) were used to fill-up the tubes without introducing air bubbles. The needles were cleaned with trichloroethylene and with acetone in an ultrasonic bath, then rinsed, dried and burnt to red point.

TABLE I Physical constants: surface tension γ; density, ρ; dynamic viscosity, μ; and temperature, T

Liquid	γ ($\mathrm{mN\,m^{-1}}$)	ρ ($\mathrm{kg\,m^{-3}}$)	μ (cP)	T (°C)
Heptane	20.3	680	0.409	20
Octane	21.6	700	0.542	20
Dodecane	25.4	766	1.53	21
Hexadecane	27.3	775	3.47	21
Squalane	29.2	809	26.81	21
Nitroethane: pure	32.3	1040	0.64	22
+ Tween	31.7	1040	0.64	22
+ DTAB	32.5	1040	0.64	22
Oil B	32.5	875	200	21
Oil S	29.3	876	38	21
Oil T	30	840	39	45
Emulsions				
B 10%		~1000	2	22
B 5%		~1000	1.7	22
B 3%		~1000	1.5	22
B 1%		~1000	1.3	22
S 10%		~1000	3.5	22
S 5%		~1000	1.9	22
S 3%		~1000	1.5	22
S 1%		~1000	1.3	22

For each tube, a specified mass of powder was weighed: e.g. 0.66 ± 0.005 g steel powder and 0.20 ± 0.005 g iron oxide powder, except when otherwise specified. These masses occupy, without compacting, one-third of the tube volume. The tubes were then carefully filled with chosen liquids and well capped; they were shaken first manually then in an ultrasonic bath for 30 min to suspend the powder as homogeneously as possible in the liquid medium. Eventually, the sedimentation height, H, could be measured as often as necessary against time until no further change in H occurred. The evolution with time of the supernatant was also observed. Unless mentioned to the contrary, all the experiments were performed at room temperature (~21 °C) and each liquid–powder system was tested at least twice.

2.3. Experimental difficulties

There are two main reasons for the scatter of the results, in spite of the rigorous experimental procedure.

(i) Ultrasonic stirring which was used to break powder aggregates, was efficient in pure industrial oils and in oil/water emulsions, but not always so in alkanes or nitroethane where the formation of agglomerates could be observed: these agglomerates could inhibit the sedimentation by friction along the walls and by formation of particle-free liquid cavities.

(ii) With emulsions at low oil concentrations there is some hydrogen emission due to water electrolysis because of the variety of metals in the steel particles. This emission can be strong enough to cause the expulsion of the tube tap so that no further measurement can be done.

3. Results

Initially the system is an homogeneous colloidal suspension. When the particles settle, they form aggregates by colliding with other particles and other aggregates which can be stabilized by long-range interaction forces and broken by hydrodynamic stresses generated by the relative motion [7]. In a sedimentation

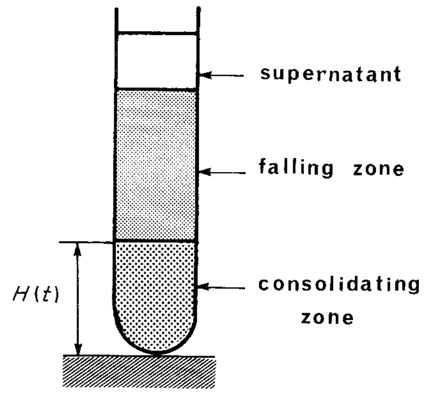

Figure 2 The three zones of sedimentation.

tube three zones can generally be distinguished (Fig. 2).

(i) The supernatant which is usually particle-free. However, with emulsions, if the particles collide, they may be surrounded preferentially by oil cells, decreasing their apparent weight and separating the oil and water phases; some particles may then float at the liquid surface.

(ii) The falling zone where the suspension is actually settling; it is also strongly reorganizing due to the particle–particle and/or liquid–particle physicochemical interactions and viscous dissipation. Various configurations can be observed: formation of gels (oxide powder in emulsions), formation of almost spherical dense aggregates, formation of loose aggregates, etc. . . . This zone is disappearing when the suspension has totally settled.

(iii) The consolidating zone which can evolve for a very long time, from 1 min to several days, even months.

The equilibrium height, H_s, is the result of the particle packing. From a pure geometrical point of view, two situations can be encountered. If the aggregates are homogeneously and regularly packed, a smaller volume is obtained when the interparticle distances are minimized. Minimal distances can be achieved when long-range repulsive forces are screened by surfactant adsorption on to the particles, for example. If, on the contrary, the aggregates are forming stable agglomerates which are not broken by the viscous stresses during sedimentation, these agglomerates do not compact properly and there remain many particle-free spaces which increase the final volume even if the interparticle distances are very small inside the aggregates.

The aspect and extension of each zone, and the lifetime of the falling zone are strongly dependent on the suspending liquid and the nature of the solid (steel or oxide powder in the present case) and will be discussed below; the limit between two contiguous zones may or may not be sharp. Further interest is stimulated by the sedimentation rate $\mathrm{d}H/\mathrm{d}t$; however, we have rather plotted, whenever possible, the quantity $A = (\mathrm{d}H/\mathrm{d}t)/[g(\rho_s - \rho_L)/\mu]$ against time where g is the gravity acceleration and ρ_s and ρ_L are the respective densities of the solid and liquid constituents; it is proportional to the square diameter of the aggregate. The linear dependence on the liquid viscosity and the apparent weight has thus been eliminated and the influence of the aggregation has been emphasized.

In general, three phases of the process can be distinguished.

(i) $0 < t < t_A$: *aggregation phase.* The front is very diffuse and no sedimentation rate can be measured nor plotted. The suspension is aggregating because of collisions due to Brownian motion which is partly dissipated by the liquid viscosity.

(ii) $t_A < t < t_s$: *sedimentation phase.* The front between the supernatant and the falling zone is sharp and, usually, $A(t)$ has a plateau, i.e. the sedimentation rate is constant, thus there is no bottom effect in this phase and either the aggregates are not ruptured during settling, or the aggregation and disaggregation rates balance.

(iii) $t_s < t < t_\infty$: *consolidation phase.* After t_s, the sedimented volume is essentially consolidating; the time asymptotic behaviour of $A(t)$ is usually a power law $A(t) \propto 1/t^\alpha$, where α is an empirical constant.

These three phases of the sedimentation process are not always measurable; nevertheless their distinction provides a general framework to the following discussion:

3.1. Results with non-emulsified liquids

First of all, a good linear dependence between the final sedimentation height, H_s, and the mass of solid particles was actually verified for two pairs of the same powder and oil within experimental error (Fig. 3a and b).

3.1.1. Non-industrial liquids

Rough data on the sedimentation height, H, with time are displayed in Fig. 4a and b for various alkanes and nitroethane saturated with water. Apart from the nitroethane, which will be discussed below, there is an

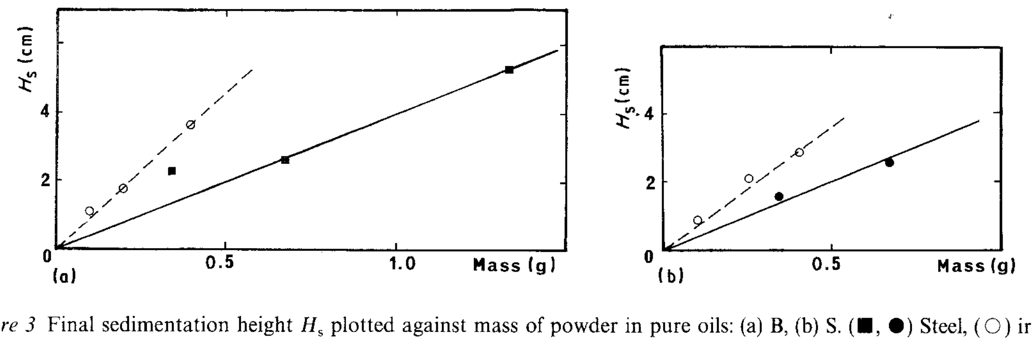

Figure 3 Final sedimentation height H_s plotted against mass of powder in pure oils: (a) B, (b) S. (■, ●) Steel, (○) iron oxide.

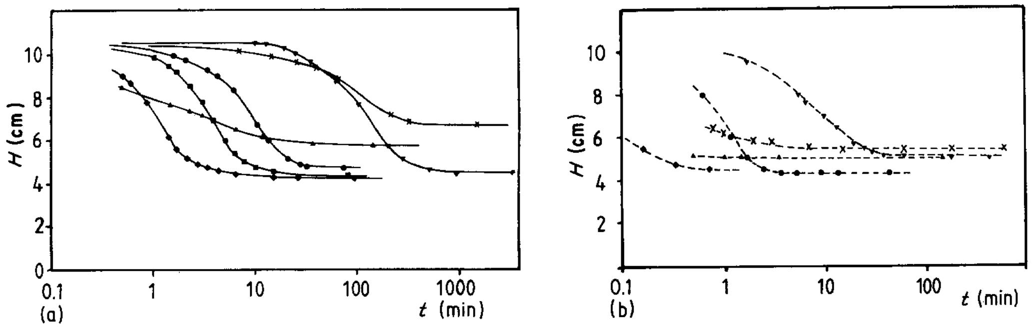

Figure 4 Sedimentation height H plotted against time for various alkanes and nitroethane. (a) Steel, (b) iron oxide. (▲) Heptane, (◆) octane, (■) dodecane, (●) hexadecane, (▼) squalane, (×) nitroethane.

obvious influence of the viscosity on $H(t)$: the more viscous the oil, the lower the sedimentation rate; liquids with comparable viscosities give comparable results in these semi-log plots.

The sedimentation rate was measured graphically in Fig. 4a and b and then A was plotted in Fig. 5a and b. With apolar surfactant-free liquids, such as the series of homologous unbranched alkanes (C_8 to C_{16}), the powder forms visible dense almost spherical aggregates (due to Van der Waals attraction), which are not broken by the motion if the viscosity of the liquid is very low. The larger aggregates are obtained with the oxide powder which settles much faster than the steel one, in spite of an unfavourable gravity influence.

The sedimentation phase exists only with steel powder for heavier alkane and the consolidation phase always exists. The three phases are only observed for squalane (branched alkane): its rather high dynamic viscosity hinders the particle mobility and aggregation for about 10 min. It should be noticed that the final volumes of sedimentation are equal whatever the alkane, within experimental error (Fig. 4a and b).

The polar nitroethane saturated with water gives essentially the same results as the light alkanes (very short aggregation time, same final volume) with the iron oxide powder (Fig. 4b). This is not true for the steel powder: aggregation is much slower ($t_A \sim 10$ min) and the final volume is much higher than the previous one. There are some double-layer effects due to the presence of ions in the liquid which hinder considerably the aggregation and increase the final volume.

The presence of surfactants in pure liquids can modify drastically the previous behaviour although it has little influence on the surface tension value (Table I). Final sedimentation height has been measured in nitroethane with two surfactants (cationic DTAB, non-ionic Tween 20) at various concentrations between 10^{-4} and 10^{-1} M. Results are shown in Fig. 7.

3.1.1.1. Steel powder. (Figs 6a and b, and 7). Its aggregation and sedimentation are not influenced by dissolution of DTAB in any of the two solvents, alkane (Fig. 6a) and nitroethane saturated with water (Fig. 6b), whatever the concentration (Fig. 7); they are slightly influenced by dissolution of Tween 20 in nitroethane (Figs 6b, 7) and strongly by dissolution of Tween 20 in alkane (Fig. 6a). Hence, in both solvents, the cationic DTAB does not seem to be adsorbed on steel which is mainly positively charged, while the non-ionic and hairy-shaped Tween 20 is easily adsorbed on it: moreover the Tween tails are then occupying a large volume around the particles in alkanes stabilizing the suspension probably by steric repulsions and increasing the final sedimentation volume. This does not occur in nitroethane which is probably too polar to allow the tail effect.

3.1.1.2. Iron oxide powder. When it occurs, sedimentation is very fast (less than 1 min): as a general law, the aggregation phase is almost instantaneous but the final volumes of sedimentation are quite different for the various suspending liquids.

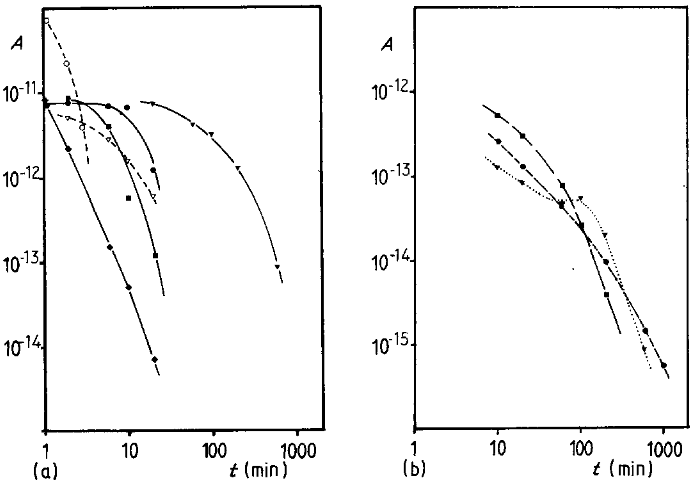

Figure 5 Sedimentation rate $A = (dH/dt)/[g(\rho_s - \rho_L)/\mu]$ (m^2) plotted against time for: (a) various alkanes; (◆) octane, (■) dodecane, (●, ○) hexadecane, and (▼, ▽) squalane with steel (solid symbols) and iron oxide (open symbols); and (b) nitroethane with steel powder, (▼) pure, (●) with DTAB ($C = 3.8 \times 10^{-2}$ M), (■) with Tween 20 ($C = 1.5 \times 10^{-2}$ M).

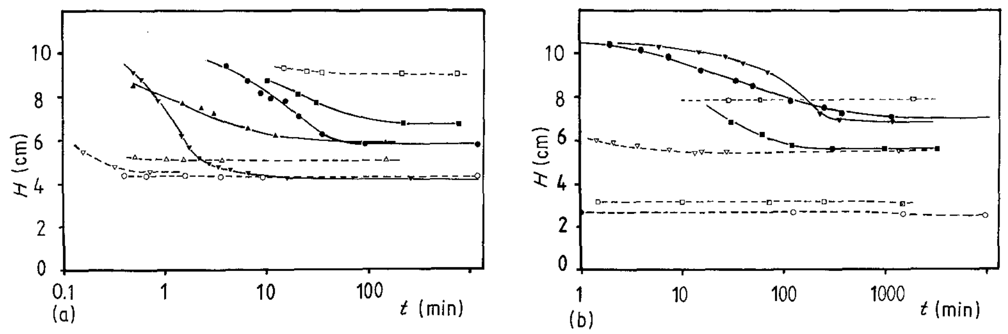

Figure 6 Influence of surfactants on sedimentation height with time, with steel (solid symbols) and iron oxide (open symbols). (a) (▲, △) Heptane, (●, ○) heptane + DTAB ($C = 2.2 \times 10^{-2}$ M), (▼, ▽) octane, (■, □) octane + Tween 20 ($C = 7.9 \times 10^{-3}$ M). (b) (▼, ▽) Pure nitroethane, (■, □) nitroethane + Tween 20 ($C = 1.5 \times 10^{-2}$ M), (●, ○) nitroethane + DTAB ($C = 3.8 \times 10^{-2}$ M).

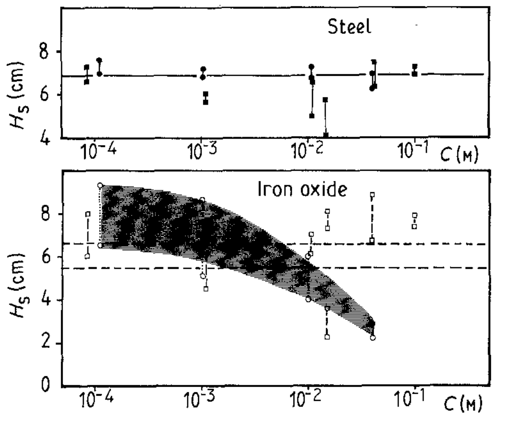

Figure 7 Final sedimentation height H_s plotted against surfactant concentration in pure nitroethane with (——) steel, (------) iron oxide, and in nitroethane (■, □) with Tween 20 (■) steel, (□) iron oxide, and (●, ○) with DTAB (●) steel, (○) iron oxide.

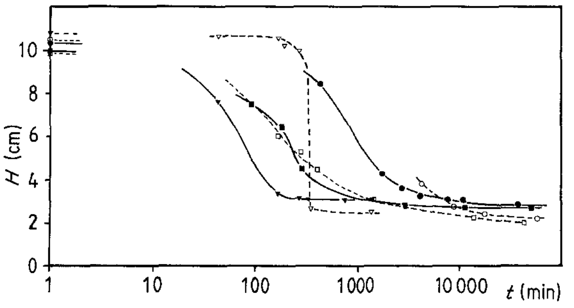

Figure 8 Sedimentation height H plotted against time in industrial oils (●, ○) B, (■, □) S and (▼, ▽) T, for steel (solid symbols) or iron oxide (open symbols).

Again DTAB has no effect when it is dissolved in alkanes (Fig. 6a) (actually little DTAB can be dissolved in an alkane [8]) but it has a strong effect in nitroethane (Fig. 7): in this case the final sedimentation height decreases below the value obtained with the alkanes as the DTAB concentration increases: DTAB is then adsorbed on the negatively charged sites of the iron oxide powder screening them and preventing double-layer repulsions to occur.

Tween 20 has usually a strong stabilizing effect preventing sedimentation when it is dissolved in a light alkane (Fig. 6a) or in nitroethane (Figs 6b and 7). However, with one solution of Tween 20 in nitroethane the final volume of sedimentation was much lower than in other experiments, while the aggregation process was almost immediate. This amazing behaviour may be due to the formation of very compact aggregates.

3.1.2. Industrial oils

For pure industrial oils, the three previous phases exist in general for both powders. However, at the beginning of the sedimentation experiment, the suspension is very opaque and visual observations are extremely difficult, even impossible.

For the steel powder, a sedimentation front is only visible after about 50 to 100 min with the S and T oils (Fig. 8) and their evolution with time follows the results obtained with squalane which has a comparable dynamic viscosity, reasonably well (Fig. 4a); in B oil which is about five times more viscous, the front is visible after ~500 min. Viscous stresses, which are presumably quite high, seem to enhance the disaggregation process hindering fast sedimentation.

Iron oxide sedimentation in S and B oils is similar to that of steel while, usually, in the pure liquids investigated above, it was much faster despite the lower density: the aggregation process was comparatively more hindered in industrial oils (note that measurements are almost impossible in B oil). This effect is even more striking with T oil (Fig. 8) where the suspension is stable for about 300 min before it rapidly settles. Such a stabilization of the suspension was also observed above, in a light alkane with Tween 20 (Fig. 6a) and was attributed to steric repulsion: then the suspension did not settle contrary to the present case.

As already claimed, industrial oils have an unknown composition and it is difficult to understand this long-term behaviour.

The final volumes of sedimentation are all equal whatever the oil for the same powder and they are always smaller than those obtained with pure alkanes. We have already seen that the aggregation rate is smaller with industrial oils; moreover the packing is more efficient. It is probably due to the fats contained in the oils which wet the powders fairly well.

3.2. Results with industrial emulsions

In the rolling mills, the oil concentration of the cooling emulsion usually ranges between 2% and 6% depending on the oil. Sedimentation experiments were repeated with emulsions of various concentrations, and the previous discussion can essentially be transposed.

However, emulsions introduce water as a new phase, and this has three consequences.

(i) The stability of the emulsions during the sedimentation process must now be considered for the applications we have in mind.

(ii) With steel powder there is some hydrogen emission.

(iii) Oil and water do not have the same wetting properties.

3.2.1. Emulsion breakdown

First of all, it was checked that the ultrasonic stirring did not change the stability of the particle-free emulsions; B and S oils give stable emulsions and T oil gives a metastable one. During the filling of the tubes, the oxide powder easily imbibed the emulsions; on the contrary, with steel powder, in emulsions as in pure water, a strong repulsion occurs between liquid and solid phases (Fig. 9), and only an ultrasonic bath can mix these two parts and often breaks the emulsions. After settling of the oxide powder, the supernatant was turbid although clearer than the initial emulsion, whereas for steel, the supernatant became as limpid as water. Micrometre-sized solid particles are supposed to stabilize oil/water (O/W) emulsions by adsorbing at the liquid–liquid interface if their surface energy is favourable. This occurs except if a suitable agent decreases the solid concentration at the oil/water interface causing the solid particles to aggregate with each other [9].

Actually, the S and T emulsions were always broken by both powders whatever the oil concentration (below 10%) for the given mass (0.66 g steel powder and 0.20 g iron oxide); the B emulsion was broken for concentrations below 5% with steel, and below 3% with oxide. In addition, during settling of the iron oxide powder, several superimposed pink rings are formed which disappear after a long time; this is due to a slight flocculation of the particles in networks of various concentrations.

No measurement can be made on T emulsions; however, some qualitative observations can be made: the column breaks and two very stable tops are formed; one falls, the other one floats. They are not destroyed by manual shaking.

3.2.2. Rate of sedimentation

The rates of sedimentation are again strongly dependent on the oil and powder nature and on the oil concentration.

3.2.2.1. Steel powder. (Figs 10 and 11.) As a general law, when the oil concentration of the emulsion is below 3%, the experiments are difficult to perform and are poorly reproducible because of hydrogen emission: they are even impossible with T oil which is solid at room temperature and has to be used at 55 °C.

Increasing the oil concentration increases considerably the aggregation and sedimentation rates in spite of a slight increase of the dynamic viscosity (Figs 10 and 11, Table I). For large oil concentrations, the final volume of sedimentation is reached in 5 min with the 10% B emulsion and in 2 min with the 10% S emulsion. The aggregation time is even reduced when the half-mass of powder is used, i.e. when the oil content relative to the solid volume is increased. Everything proceeds as if the only role of water is to decrease the dynamic viscosity compared to pure oils: very large aggregates are indeed observed which are not destroyed by viscous dissipation and which settle very quickly.

When the oil concentration is below 3%, one must be cautious in interpreting the results because of their dispersion. However, there are general trends: the lower the oil concentration, the slower is the sedimentation rate, and the higher the final sedimentation volume. It seems that the aggregation rate is limited by the total amount of oil. With a poor emulsion there are insufficient surfactants to saturate all the active sites of the powder and to stabilize the aggregates strongly enough.

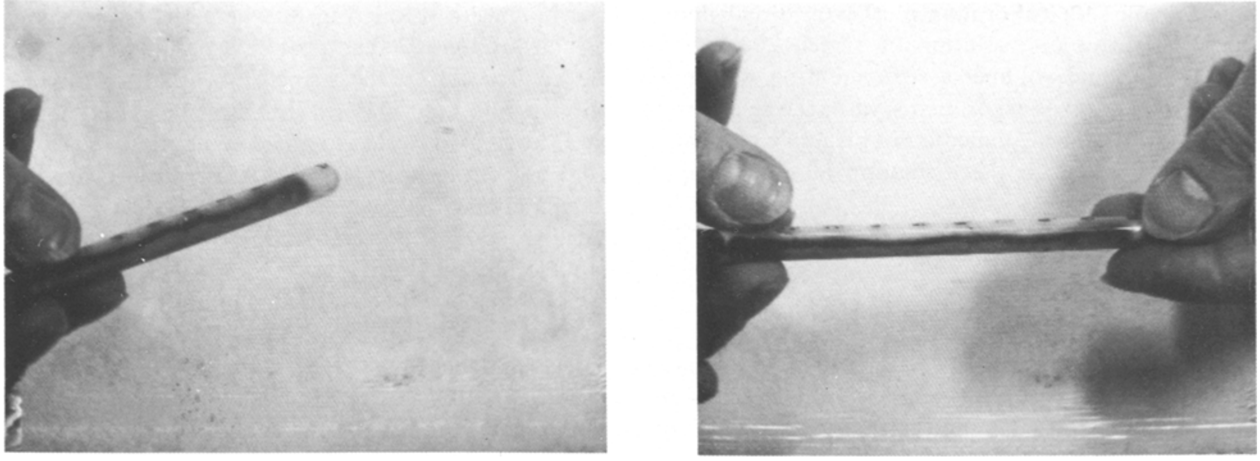

Figure 9 Repulsion between solid and liquid phases during imbibition (steel powder in the presence of S emulsion 2%).

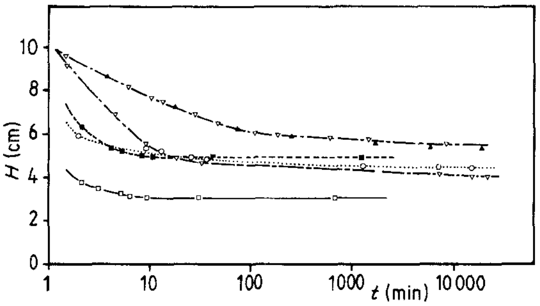

Figure 10 Sedimentation height H plotted against time: steel powder in B-emulsions (□) 10%, (■) 5%, (▽) 3%, (○) 2%, (▲) 1%.

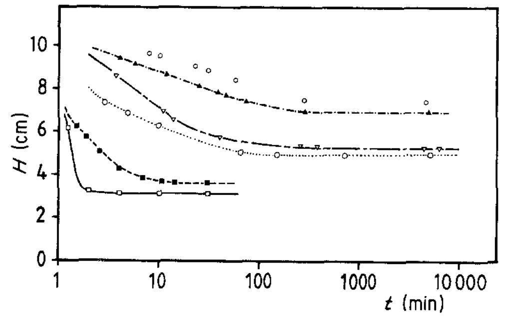

Figure 11 Sedimentation height H plotted against time: steel powder in S emulsions. For key, see Fig. 10.

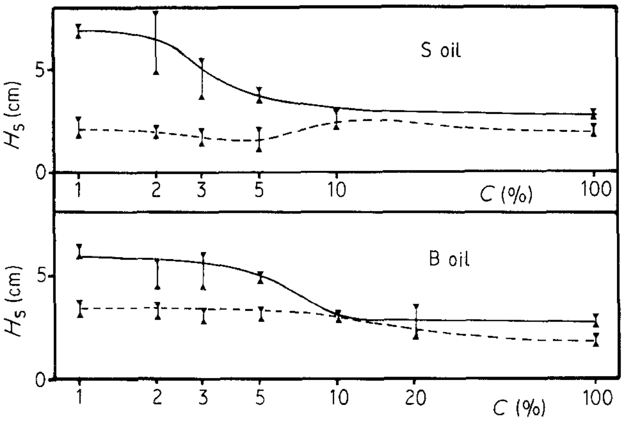

Figure 12 Final sedimentation height H_s plotted against oil concentration for S and B emulsions.

The final volume of sedimentation of a given mass of powder is plotted as a function of the oil concentration in Fig. 12: it shows a typical saturation behaviour for both oils.

This effect is confirmed as the mass of powder is changed: results are plotted in Fig. 13 with non-dimensional quantities. H_s is scaled by the final sedimentation height, H_0, of the same mass of powder in the pure oil, and θ is the ratio of the oil to the powder volume.

3.2.2.2. Iron oxide powder. Results are strongly dependent on the nature of the oil (Fig. 14).

The S emulsions below 10% are always broken after shaking in an ultrasonic bath, whereas for a rich emulsion (at 10%) there is a formation in the supernatant of a pink colloidal suspension which disappears the following day (the liquid is then limpid). In both cases, there is a formation of small and regular aggregates which settle very quickly. The final volume of sedimentation is reached within 1 min; it is almost

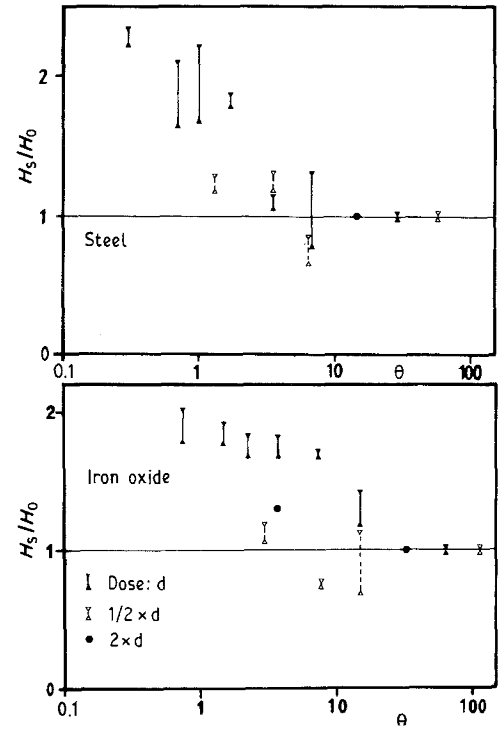

Figure 13 Non-dimensional sedimentation height H_s/H_0 plotted against θ.

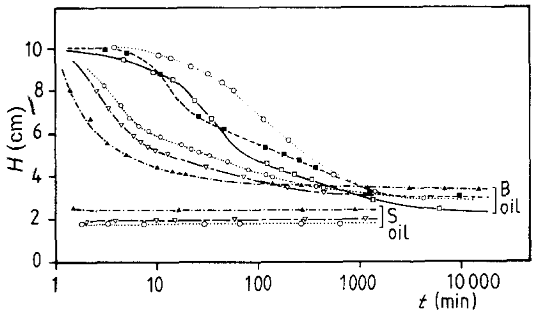

Figure 14 Sedimentation height H plotted against time: iron oxide powder in B and S emulsions. For key see Fig. 10.

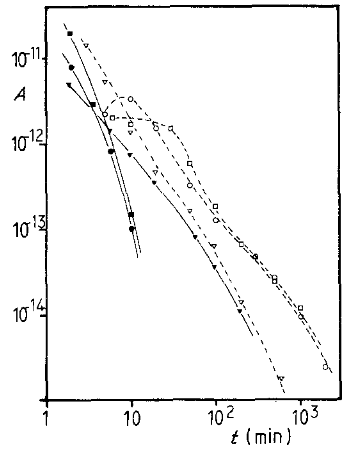

Figure 15 Sedimentation rate $A = \mathrm{d}H/\mathrm{d}t$ (m^2) plotted against time for B emulsions, with iron oxide (open symbols) and steel (solid symbols); (▽, ▼) 3%, (○, ●) 5%, (□, ■) 10%.

independent of the oil concentration and equal to the volume measured in pure S oil. A small amount of oil is sufficient to saturate all sites. Eventually there is some similarity with the behaviour observed with iron oxide powder in nitroethane with DTAB.

The B emulsions give totally different results: the 5% and 10% emulsions and some of the 2% and 3% ones are not broken during the process, there is a plateau on the aggregation curve (Fig. 15), there are no visible aggregates and the settling takes much more time, the viscous stresses are probably large enough to limit the aggregation rate. There is no obvious saturation effect (Figs 12, 13b) with respect to the oil concentration.

4. Conclusion

For the steelmaking industry these simple sedimentation experiments can provide a novel and useful homologation test. As already emphasized the oils composition is unknown for obvious commercial reasons, but we know from the steelmaker that the B oil rolls fairly well with acceptable reduction rate, the S oil does not work properly, the T oil rolls very well, accepts a large reduction but the plate is very dirty.

The sedimentation tests have provided two major pieces of evidence:

(i) the S and T emulsions are always broken by the steel particles,

(ii) the sedimentation rates are faster with S than with B emulsions at a same oil concentration.

Hence, the additives and fats dissolved in the S and T oils are more easily adsorbed on the steel particles than those dissolved in the B oil and they induce a stronger aggregation of the powder. There is also a subsequent decrease of the "free" surfactants which are no longer sufficient to maintain the emulsification.

The formation of larger aggregates should not be *a priori* so unfavourable, because they settle better and they can be more easily eliminated by the magnetic filters; however, the excessive demulsification constitutes a real drawback for the rolling mills through which the rolling emulsion is recirculated.

This test is not sufficient to appreciate the oil quality with regard to its interaction with the steel. In a companion paper [10] we propose other experiments to study the spread of emulsions on the plates.

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References

1. M. G. VUCICH and M. X. VITELLAS, *Iron Steel Eng.* Dec. (1976) **29**.
2. C. H. TURNER, "Development of steel cold rolling lubricants to meet the challenge of the Eighties", Proceedings of Conference on Advance in Cold Rolling Technologyy, Imperial College, 17–19 September, 1985.
3. E. I. VARGHA-BUTLER, T. K. ZUBOVITS, H. A. HAMZA and A. W. NEUMANN, *J. Dispersion Sci. Technol.* **6** (1985) 357.
4. A. MARMUR, *Adv. Colloid Interface Sci.* **19** (1983) 75.
5. D. DUNSTAN and L. R. WHITE, *J. Colloid Interface Sci.* **111** (1986) 60.
6. J. T. DAVIES and E. K. RIDEAL, "Interfacial Phenomena" (Academic Press, New York, 1961) p. 43.
7. P. M. ADLER, *AICHE J.* **25** (1979) 487.
8. M. MAHE, Doctoral Dissertation, Université de Paris VI (1987).
9. V. B. MENON and D. T. WASAN, *Colloids and Surfaces* **29** (1988) 7.
10. B. PRUNET-FOCH, F. LEGAY-DESESQUELLES and M. VIGNES-ADLER, companion paper (1990).

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