

TURBULENT SETTLING (TS) TECHNOLOGY FOR SOLVENT EXTRACTION

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1. INTRODUCTION

The distribution of local turbulent energy dissipation rates in the agitators of traditional mixer-settlers is extremely non-uniform.

Bateman Advanced Technologies Ltd., together with Turbulent Technologies Ltd. have developed new technology for faster and more complete separation of liquids in solvent extraction plants and in particular - for decreasing organic entrainment in the aqueous phase.

We replace the agitator of the final mixing stage tank with a special mixing system that generates optimum turbulence distribution for efficient coalescence of the smallest droplets onto the surface of large and medium size droplets of the disperse phase.

This leads to a significant reduction in the number of small droplets that negatively affect both the speed and the efficiency of phase separation

Generation of the optimal turbulence conditions is based on predictions from a mathematical model of drop breaking and coalescence in turbulent flows developed earlier by Braginsky and Kokotov [1-4]. The model has been tested across a wide range of concentrations and physical properties of different liquids and mixing conditions.

Pilot tests conducted at the Lady Annie copper extraction plant in Australia showed an approximately 50% decrease in separation time and a 3-5 times decrease in organic entrainment in aqueous phase, for both the extraction and the stripping batteries.

TS technology can be retrofitted to existing plants, or designed-in to new SX plants. In addition to a reduction of losses of expensive extractants, the TS technology will reduce organic contamination of the product and decrease the maintenance costs of filters, as well as enabling increased production rates for existing extraction plants. New plants can be built with reduced settler volume, saving capital and operating expenses.

2. BREAK UP AND COALESCENCE OF DROPS IN MIXED VESSELS

Basic physical mechanisms and simplified (mono-dispersion approximation) mathematical model of the process of emulsion formation in turbulent flows in mixing tanks have been developed by L. Braginsky and Y. Kokotov [1]. The model predicts the frequency of two simultaneous processes - the break up of droplets and the coalescence of droplets, under the effect of turbulent pulsations, and it takes into account actual non uniform distribution of turbulent energy in the mixing tank.

For mono-disperse approximation the number of drops in a liquid-liquid system with defined physical properties and constant volume fraction of the disperse phase may be considered as a function of mixing intensity and process time. Its change, starting from some initial size, in a volume with non-uniform distribution of turbulence may be described by equation:

$$\frac{dd}{d\tau} = \frac{d}{3V} \int_v (N_c - N_b) dV, \quad (1)$$

where d is diameter [m].

To use this equation, three functions should be known. Two functions, frequency of coalescence and frequency of breaking, N_c and N_b , depend on the drop size, physical properties of the phases and the local rate of turbulent dissipation of energy, whilst the third function - distribution of turbulent energy dissipation $\varepsilon = P/(\rho V)$, depends on the macro-scale flow pattern in the mixing tank.

2.1 THE FREQUENCY OF BREAKING

According to the results of recent studies in the kinetics of drop break-up in mixing vessels in the absence of coalescence [2-4], a quantitative description of drops break-up may be based on the universally known Kolmogorov's stability condition for a drop in a turbulent flow. An individual act

of deformation and breaking must be assumed to occur under action of an instant velocity pulsation in the vicinity of the drop on the condition that the amplitude of the pulsation exceeds a certain minimum value v^* . The relation between this "critical" value and the mean square root velocity was estimated as

$$U^* = \frac{v^*}{v} = \frac{0.775}{\varepsilon^{1/3} d^{1/3}} \left(M/d + \sqrt{\left[(M/d)^2 + \frac{10\sigma}{\rho_c d} \right]} \right), \quad (2)$$

where

$$M = \left| 1.2 \frac{\rho_d}{\rho_c} v_d - 3v_c \right|, \quad (3)$$

σ is interfacial surface tension [N/m].

The linear scale of the "destructive" pulsations was estimated as $L = 2.17 d$ - the minimum length of the deformed droplet, corresponding to the loss of stability. Within the framework of this model, the mean frequency of drops breaking in an area with the local turbulent dissipation ε may be estimated as

$$N_b = f_l P(v' \geq v^*) (1 - P(0)), \quad (4)$$

or $N_b =$ mean frequency of pulsations of the scale L multiplied by relative frequency of pulsations L with amplitudes $v' \geq v^*$ and multiplied by x probability of one or more droplets residing in an area of the scale L ,

where
$$f_l = \frac{1}{l^3} \frac{\varepsilon^{1/3}}{l^{2/3}} \quad (5)$$

$$P(v' \geq v^*) \cong \sqrt{2/\pi} \int_{U^*}^{\infty} \exp(-U^2/2) dU, \quad (6)$$

and
$$P(0) \cong 1 - \exp(-19.6\varphi) \quad (7)$$

According to the above equations (1– 7) the frequency of drop breaking depends on the local energy dissipation energy, drop diameter, interfacial surface tension and viscosities of both liquids formatting emulsion.

2.2 THE FREQUENCY OF COALESCENCE

The act of coalescence is usually assumed to occur (see for instance [5]) if two droplets approach each other and collide and the collision happens to be "efficient", i.e. the amplitude of the fluctuation is high enough to overcome the resistance of a liquid film separating the drops:

$$N_c = \text{frequency of collisions multiplied by efficiency of collisions}$$

It seems, however, that the individual acts of collision and merging of the drops must not necessarily occur due to the same random turbulent fluctuation. The necessary condition of coalescence of two droplets may thus be assumed to consist in their being in contact as the fluctuation occurs. The term "in contact" here means that the distance between the drops' centers is practically equal to the drop diameter, d , and their surfaces are separated by a thin layer of ions existing on the water-oil boundary, water side. According to the postulates of the DLFO-theory [6], the interfacial boundary is surrounded with a "double layer" of ionized liquid. Due to inter-action of these layers, the neighboring surfaces are kept from junction by electrostatic repulsive pressure, p . The value of this pressure depends on the chemical composition of substances. For "pure" oil – and distilled water, the theoretically estimated value is about 20 N per sq. m; it increases in emulsions stabilized with detergents, and decreases in solutions of flocculants and multivalent electrolytes. The coalescence only happens if the squeezing pulsation pressure is high enough to overcome the

repulsive pressure. The condition for a random turbulent pulsation to be "efficient" may thus be formulated as

$$v'_n \geq v_c^* = \sqrt{(2p / \rho_c)} \quad (8)$$

where v'_n is the constituent of the pulsational velocity v'_{λ} , normal to the contact surface, and $\lambda \cong d$ is the linear scale of the "coalescing" pulsations.

According to this model, mean frequency of coalescence may be defined as,

$$N_c = f_{\lambda} P(v'_n \geq v^*) (1 - P_{\lambda}(0) - P_{\lambda}(1)), \quad (9)$$

or $N_c =$ mean frequency of pulsations of the scale λ multiplied by relative frequency of pulsations with amplitudes satisfying the condition $v'_n \geq v_c^*$ and multiplied by probability of the presence of two or more drops in an area of the scale λ ,

where $f_{\lambda} = \frac{1}{\lambda^3} \frac{\varepsilon^{1/3}}{\lambda^{2/3}}, \quad (10)$

$$P(v'_n \geq v_c^*) = \frac{1}{\sqrt{2\pi}} \int_{V^*}^{\infty} \left(1 - \frac{V'}{V^*}\right) \exp(-V'^2/2) dV', \quad (11)$$

$$V^* = \frac{v_c^*}{v} = \frac{\sqrt{(2p / \rho_c)}}{\varepsilon^{1/3} \lambda^{1/3}} \quad (12)$$

and $V' = v'_{\lambda} / \bar{v}_{\lambda} \quad (13)$

The term $\left(1 - \frac{V'}{V^*}\right)$ in Eq. 11 accounts for the fact that v_n is a component of pulsation velocity normal to the contact surface.

The probability for the centers of the two drops to be in the area of the scale λ was estimated approximately as

$$1 - P_{\lambda}(0) - P_{\lambda}(1) \cong 1 - (1 + \varphi) \exp(-\varphi) \quad (14)$$

According to equations (8 – 14) the frequency of drop coalescence depends on the local energy dissipation, drop diameter, interfacial tension and viscosities of both liquids. Additionally, it depends strongly on the value of repulsing pressure and on the **emulsion concentration. The higher the emulsion concentration, the higher the coalescence intensity. In some conditions it can prevail on the breaking intensity and the drop size will increase under effect of mixing.**

The system of equations presented above allows us to describe the kinetics of drop breaking and coalescence as a function of tank and agitator geometry and properties of phases. In addition to viscosities and interfacial tension, these equations also contain one additional physical parameter - the restricting pressure of the electrostatic double layer. This model was tested in a wide range of mixing conditions and liquid properties. Comparison of experimental results with model prediction is presented in Figs. 1 -5 [1].

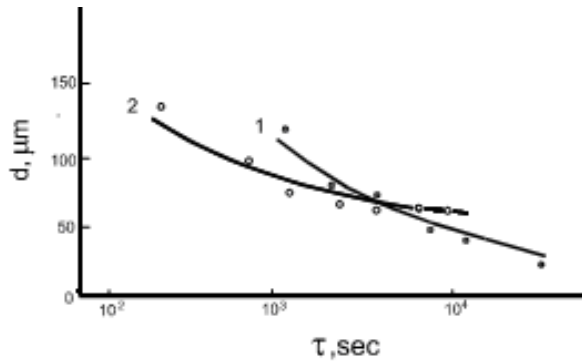


Figure 1: Kinetics of drop breaking in the absence of coalescence.
 1 - disk agitator, $\epsilon_m = 650 \text{ W/Kg}$, 2 -6-blade turbine, $\epsilon_m = 150 \text{ W/Kg}$
 Solid lines correspond to calculations by equations 1-7.

The process for a disk agitator takes much more time due to the very small volume of the high shear (maximum local energy dissipation) zone.

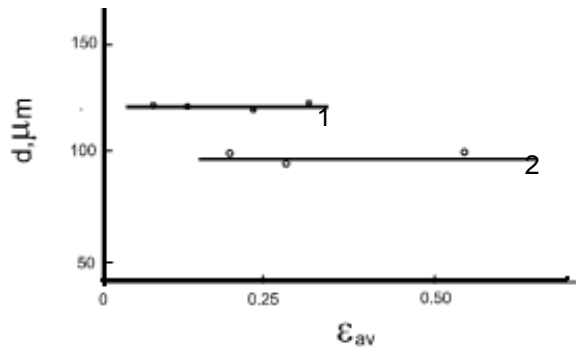


Figure 2: Break-up in the absence of coalescence: Mean drop size ("final" values) vs. specific power for different agitators.
 1 - $\epsilon_m = 30 \text{ W/Kg}$, 2 - $\epsilon_m = 60 \text{ W/Kg}$.
 Solid lines correspond to calculations by equations 1-7.

From figure 2, one can see that final drop diameter is a function of maximum value of local energy dissipation, but is not affected by ϵ_{av} .

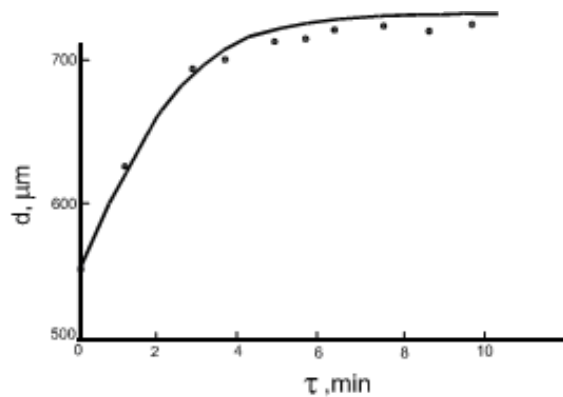


Figure 3: Kinetics of coalescence.
 Vessel volume - 4.3 l, agitator - 6-blade turbine, diameter 100 mm. $\phi=0.19$.
 Change of agitator velocity from 240 to 160 RPM at time 0.
 Solid lines correspond to calculations by equations 1-14.

Figure 3 above shows the increase of mean drop size after reducing the agitator velocity [7].

In all experiments presented in Figs 2-5, a carbon tetrachloride + kerosene solution (density 1.050 kg/cub. m, viscosity 3 cP) was used as a disperse phase. Distilled water and 0.2% solution of sulfuric acid were used as a continuous phase. Concentration of emulsions varied by 5 - 20 %. Measurements were performed using the well known light-scattering method with submerged glass fiber light conducting probe. The probe was calibrated using glass spheres of narrow size distributions. Some of the results of the measurements are presented in Figures 4 and 5. It was found that coalescence of droplets occurs not only in the most intensive turbulence area behind the agitator's blades, but also in the radial jet around the agitator. The significance of this phenomenon increases with the increase of local dissipation; it results in a smaller slope of d vs. ϵ_m curve as compared with the curves for non-coalescing conditions. This result, as well as the observed dependence of mean drop diameter on the concentration of emulsion and ϵ_m values (i.e. on the mixing conditions), was found to agree with the predictions of the equations presented above.

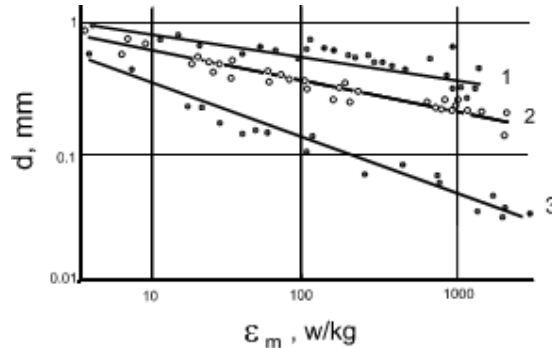


Figure 4: Break-up and coalescence. Mean drop diameter (“final” value) vs. ϵ_m .
1 - $P = 7$ Pa; 2 - $P = 20$ Pa; 3 - $P \rightarrow \infty$ (stabilized).
Solid lines correspond to calculations by equations 1-14.

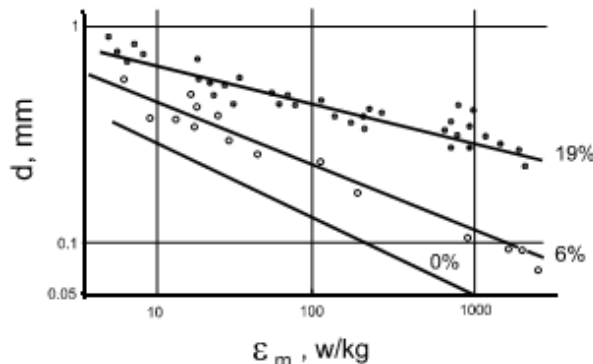


Figure 5: Break-up and coalescence. Mean drop diameter vs. ϵ_m . The effect of the concentration of the disperse phase. Solid lines correspond to calculations by equations 1-14.

3. LOCAL ENERGY DISSIPATION AND DROP SIZE DISTRIBUTION

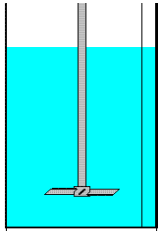
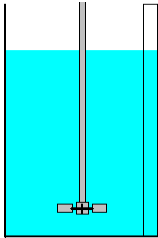
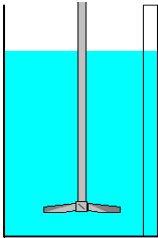
As it was shown in section 2 energy dissipation rate is a critical parameter that determines the emulsion formation and which affects the average drop size in the mixing tank. By control and optimization of the energy dissipation rate distribution, one can optimize drop size distribution with respect to the particular process requirements. In particular appropriate mixing can increase the mean drop size and decrease the number of the smallest droplets, in order to improve the separation of organic and aqueous phases in solvent extraction processes.

However in mixing tanks of traditional design, the distribution of turbulence is extremely non uniform. Table 1 presents the results of calculation for typical impellers in baffled mixing tanks using a mathematical model published in [1].

One can see that local values of turbulent energy dissipation in different zones can vary by factors of several hundred. This results in a very wide drop size distribution that is certainly not desirable in many applications, and is particularly undesirable for separation processes. In addition, the relative

zone of the most intensive mixing and correspondingly the residence time in this zone for continuous processes is very small. This means that in applications with short residence times like the mixer stages in the mixer – settlers used in hydrometallurgy, standard impellers are not efficient for the optimization of drop size distribution.

Table1. Turbulent energy distribution in typical mixing tanks

Impeller type	Drawing	Relation between maximum and averages values of local energy dissipation	Relative volume of zone of maximum energy dissipation, %
Pitch paddle		164	0.12
Disk turbine		365	0.127
Lightnin A310		547	0.03

4. THE SOLUTION FOR LIQUID EXTRACTION

Turbulent Technology Ltd. in cooperation with Bateman Advanced Technologies Ltd., developed a special mixer that provides a uniquely uniform distribution of turbulent energy dissipation across the whole volume of the mixing tank. Depending on the specific geometrical characteristics of the mixing tank, the relative maximum and average values of local energy dissipation are from 1.5-2 to 3-4 times. Theoretical calculations and experimental tests show that the optimum rotation speed of this mixer provides conditions for efficient coalescence of small droplets present in the initial emulsion onto the surface of larger drops. This significantly improves the downstream separation process in the settler - see. The required intensity of mixing has to be derived using equations 1-14 with respect to physical properties of organic and aqueous phases. That process is illustrated by figures 6 to 8.

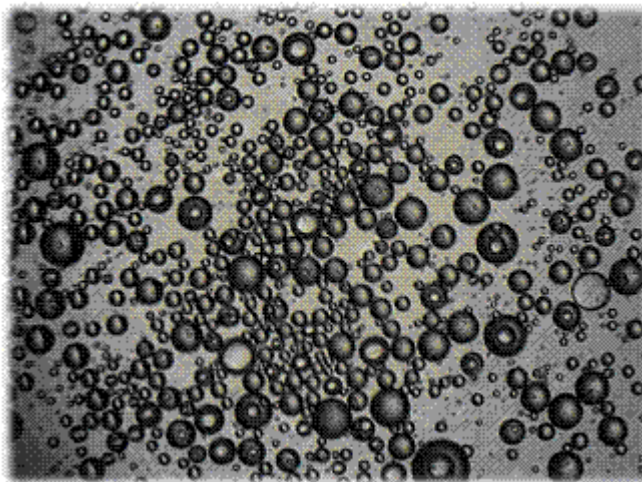


Figure 6: Initial emulsion before separation

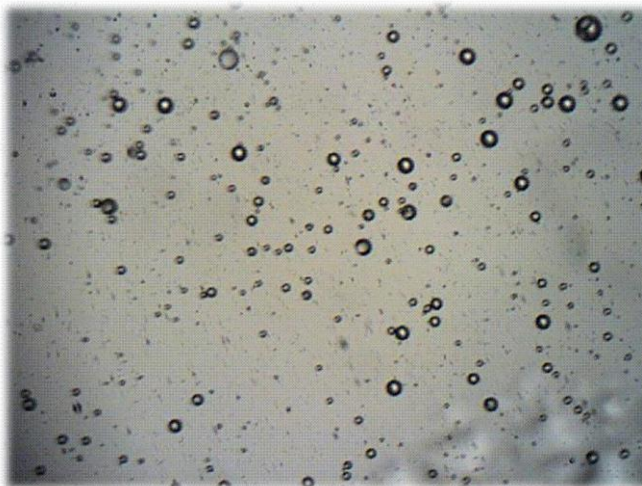


Figure 7: Organic entrainment in aqueous phase leaving settler without TS

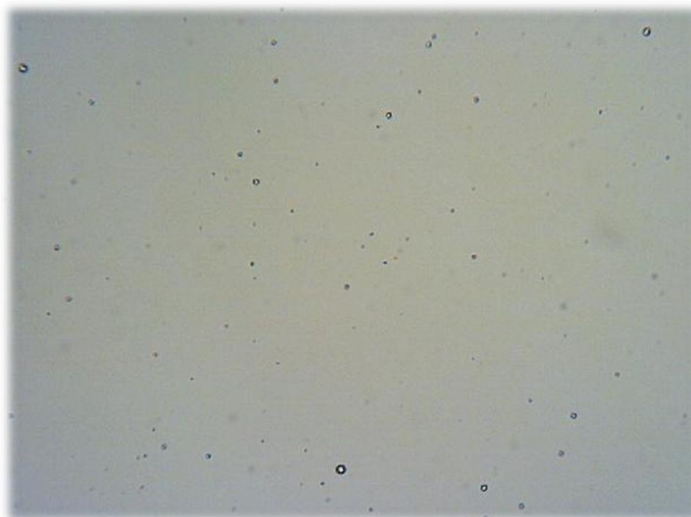


Figure 8: Organic entrainment in aqueous phase leaving settler. Initial emulsion was undergo TS treatment before entering settler

Efficient coalescence was achieved because of uniform turbulence across the whole volume of the coalescing mixer. The full volume of the mixing tank was being used efficiently to coalesce small droplets.

For retrofitting existing SX plants, the technical solution is shown at figure 9, where a TS coalescer simply replaces the last stage agitator of the existing mixer settler. In cases that more than one mixing boxes are installed, e.g. copper plants, only the agitator itself will need to be replaced and

some modifications to the mixing box, e.g. re-shape of the baffles, are needed. If only one agitator, that serves as pump mixer, is installed, second mixing box with the suitable agitator is required.

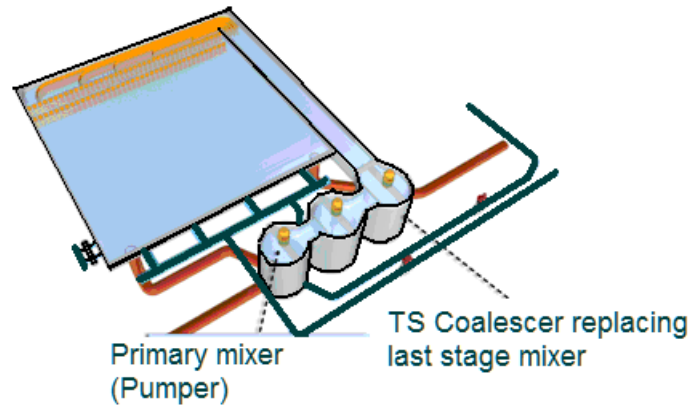


Figure 9: Bateman mixer settler, TS coalescer installed at the last mixing stage

Tailored to the characteristics of each process, the Turbulent SX agitator delivers a specific turbulent regime, which is optimized to maintain mass transfer, whilst reducing the number of small droplets that will not separate easily.

For most Liquid extraction processes in the production of copper, cobalt, nickel, uranium etc, TS technology:

- Reduces entrainment of expensive extractants
- Reduces organic contamination in the product stream
- Reduces the ecological impact of organic in the raffinate stream
- Can reduce the size of settlers needed
- Reduces maintenance costs
- Can eliminate the need for After-settles

5. PILOT TESTS

5.1 PILOT INSTALLATION

TS technology was successfully tested in November 2009 in the solvent extraction plant at the Lady Annie (LA) copper mine in Australia. A continuous pilot plant (Fig. 10, 11) included the proprietary TS coalescing agitator and Bateman settler. The emulsion flowed from the existing LA mixing tank by means of a siphon into the coalescing agitator and then was separated in the settler. Outlets of the settler were returned to the plant.

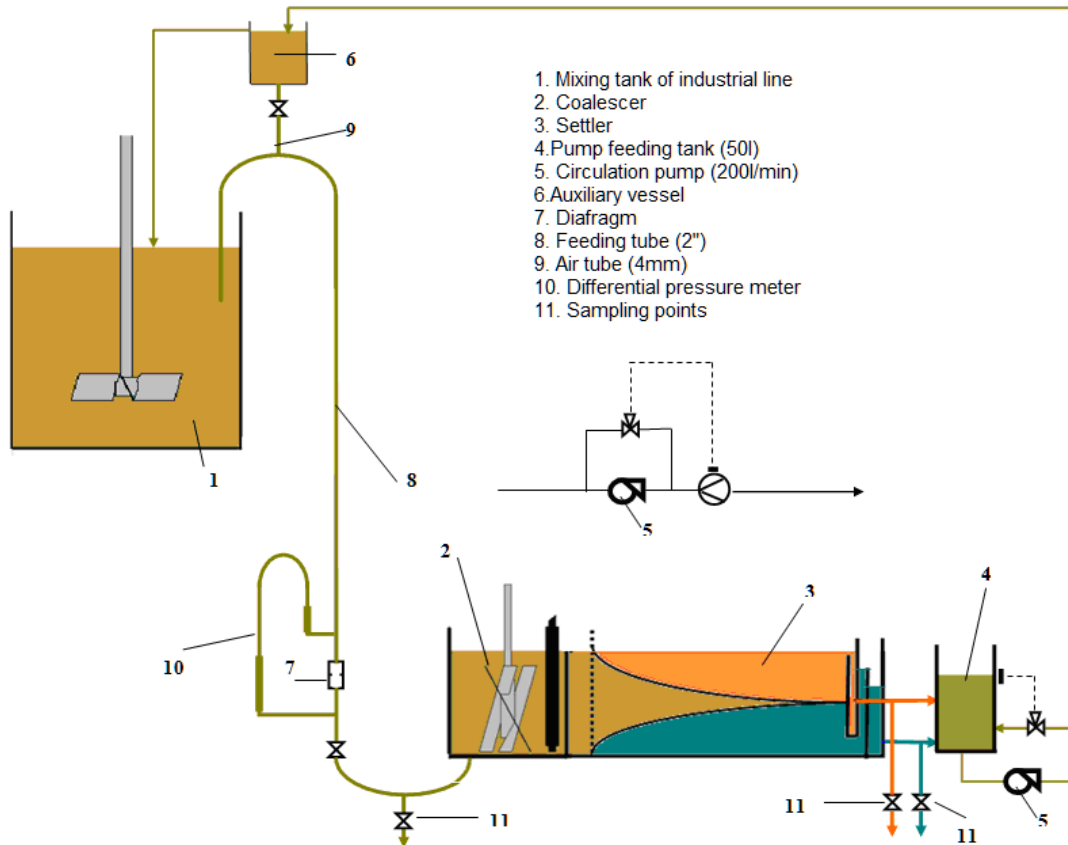


Figure10: Principal Scheme of Pilot Installation



Figure11: Turbulent Technologies Pilot Facility Lady Annie (LA) Copper Mine, Australia

Pilot tests were conducted in this manner in both the extraction and the stripping batteries.

During the test period, samples of emulsion were taken from the outlets of the existing industrial mixing tank and the pilot coalescing tank. The samples were separated in a laboratory glass settler for 5 minutes and then the entrainment of organic in aqueous phase was measured.

In parallel samples from aqueous and organic phases were taken from the outlets of the industrial LA settler (20 minutes residence time) and the Pilot settler (20 minutes residence time). Entrainment of organic in the aqueous phase was measured analytically. Samples of organic phase underwent separation in a laboratory centrifuge and then the concentration of water was estimated.

5.2 EXPERIMENTAL RESULTS

5.2.1 Organic entrainment in aqueous phase

Results of measurements of organic entrainment in aqueous phase are shown in Fig. 12 and 13. These results show that TS technology achieves a systematic significant decrease of organic entrainment at both the extraction and the stripping batteries. After treatment of the emulsion in a TS coalescer, the average concentration of organic in aqueous after settling was 5.5 ppm, as compared to 20.3 ppm without TS treatment.

It was also found that the settling mode, (batch, continuous flow in production or continuous flow in the pilot settler) does not effect organic entrainment as long as the residence time remains constant. This can be explained by the nature of the separation process. Large droplets easily separate in any correctly designed settler, while the smallest droplets with a diameter of less than 15-20 microns can not be separated and will pass through any settler. Improvement of the separation using TS technology was achieved due to coalescence of small droplets on the surface of larger ones.

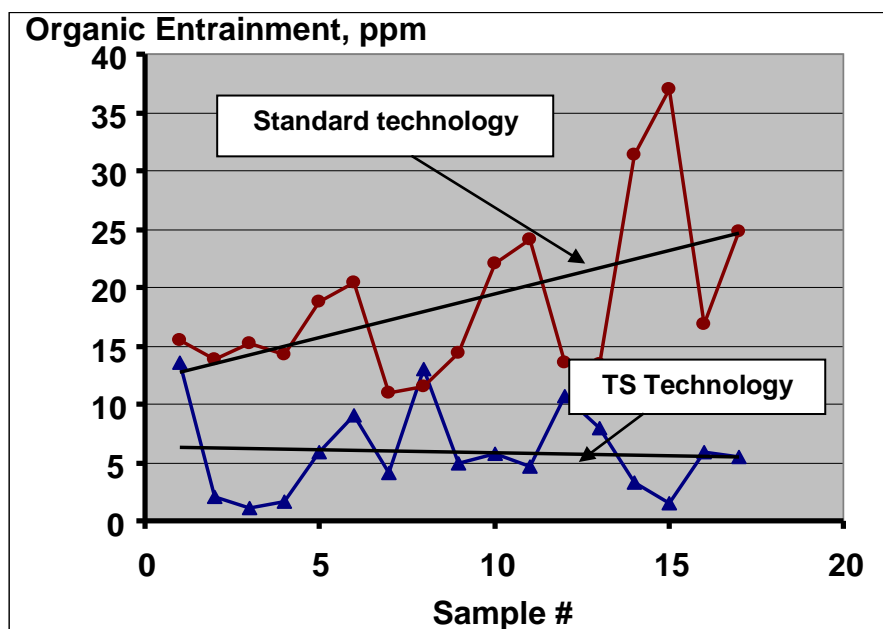


Figure12: Organic entrainment in aqueous phase after completion, Extraction battery.

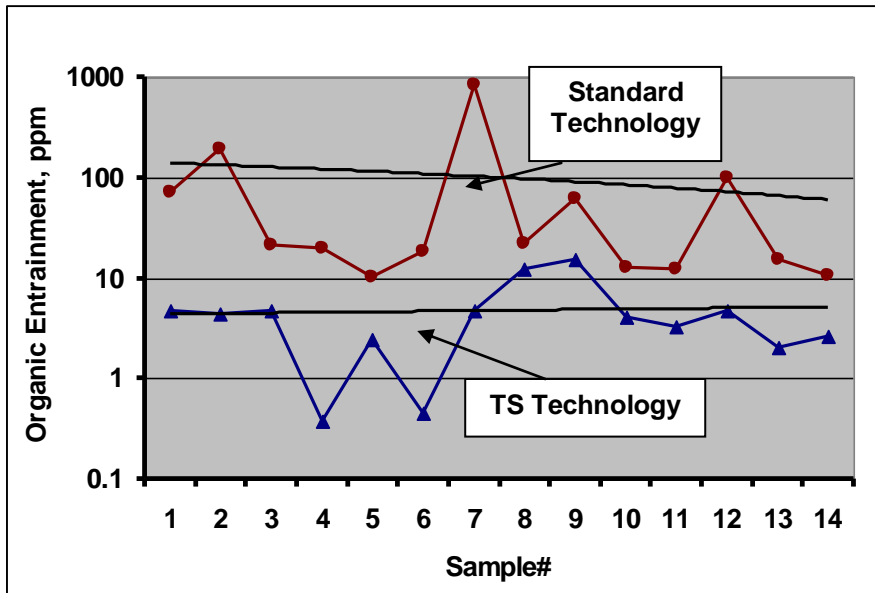


Figure 13: Organic entrainment in aqueous phase after completion, Stripping battery.

5.2.2 Aqueous entrainment in organic phase

In order to see if TS technology can influence the value of aqueous entrainments in the organic phase, samples of organic phase taken from settler outlets were separated in a laboratory centrifuge. Samples taken from the production line settler contained from 0.5% to 1% of water. No visible presence of water was found in samples of organic phase taken from the TS pilot settler outlet. This demonstrates that TS technology also improves the aqueous entrainment, decreasing the backmixing caused by it.

5.2.3 Rate of phase separation, visual tests

Improvement of drop size distribution in the TS coalescer also makes separation process in the settler much faster, see figure 14.

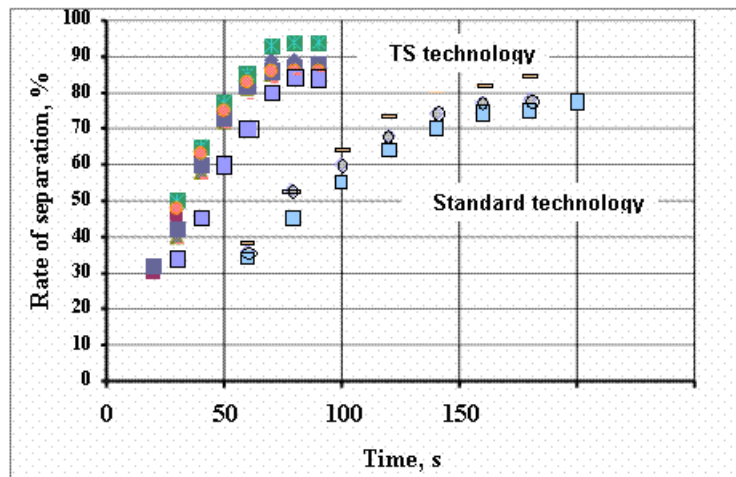


Figure14: The rate of phase separation of the dispersion (as measured in a measuring cylinder) is enhanced by the TS mixer.

As result the flux through the existing settlers may be increased, enabling either higher production rate or smaller size of the settlers without loss of effective separation.

6. SCALING UP

Because the turbulent regime is uniform and specified, scaling up is not a process of random trial and error, but simply requires recalculating the mixing conditions necessary to produce the desired turbulent regime in the larger mixing tank.

7. NOMENCLATURE

d - mean drop diameter [m]

V - volume, [m³]

N_b, N_c - frequencies of breaking and coalescence

\bar{p} - repulsing pressure [N/m²]

\bar{v} - mean sq. root pulsation velocity [m/s]

τ - time, [s]

φ - volume fraction of the disperse phase

ν_c, ν_d - kinematic viscosity of the continuous and disperse phases [m²/s]

ρ_c, ρ_d - density of the continuous and disperse phases [kg/m³]

ε - specific turbulent energy dissipation [W/m³]

ε_m - specific turbulent energy dissipation, maximum value [W/m³]

ε_{av} - specific turbulent energy dissipation, average value [W/m³]

σ - interfacial surface tension [N/m]

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