Aging of ultrasound cleaning mixtures

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Cleaning by ultrasound in perfect technologies for removal of clogging appearing in intermediate processes is very effective. Working mixtures are selected for cleaning specific silt up. They are usually pretty expensive, so in case of mass production they incur considerable costs; mixtures have to be replaced because of their quality degrading. The main reason for such degradation in the formation of the silt up. Physico-chemical aging of the mixture, caused by ultrasound radiation stimulating adverse effects is also significant. The mixture components possess different degree of resistance to a similar influence.

We are going to provide some data on qualitative changes of the water mixture occurring in a cleaning cycle and now the mixture qualities degrade after its multiple usage. For this purpose we measured simultaneously the properties of two mixture samples: one sample was evaluated after being employed in approximately 100 cleaning cycles (sample No S2), the other-freshly made (sample No S5) that has only been used in the first cycle. To eliminate influence of pollutants on mixture qualities, multiple usage was carried out "in clearance" – without dipping polluted components into the mixture. We are of opinion, that the mixture quality changes were only conditioned by physico-chemical influence of ultrasound. Hydrogen potential was chosen as a quantitative index of mixture qualities, thus employing a standard pH-meter with ESC-43-07 electrode. We made a special analysis to find out whether ultrasound doesn't cause deviation of electrode gradation, the impact was minimal and while evaluating we could take no account of the latter disturbance.

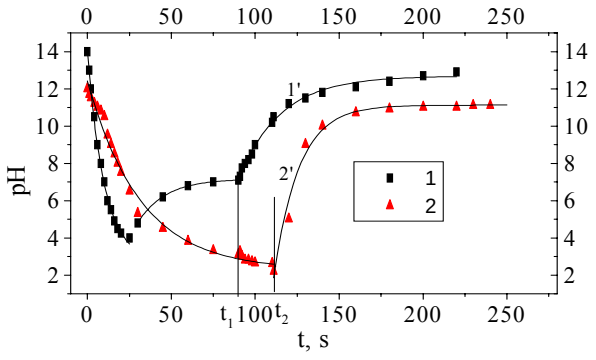

Fig. 1. **Dependency of mixture potential pH on time t at minimal overcavitational ultrasound intensity W, where 1 stands for fresh mixture S5, 2 – for used mixture S2, t_1 and t_2 – mark ultrasound turning – off moments. The points experimental data, linear the theoretically calculated.**

Evaluation results define different types of index pH dependency changes: we present here two dependency groups-time dependency and dependency on ultrasound intensity (power). One very interesting factor of electrokinetic change in ion concentration in the mixture while considering time dependency at different ultrasound intensity was observed it should be noted that ion generation and ion recombination's coefficient are dependent on ultrasound intensity. The findings will be analyzed in a more consistent way. Figure 1 illustrates hydrogen potential pH dependency on time t up to 4 minutes: 1 – of the fresh mixture, 2 – of the used mixture at minimal over cavitation ultrasound intensity. Two time moments t_1 and t_2 corresponding to the moment of turning off ultrasound radiation are marked on the axis. PH index change at the initial part of the curve is stimulated by increasing mixture acidity caused by ultrasound cavitation and deeper concentration of hydrogen ions (1) as well as by increasing electrocunductivity of the mixture. After approximately 20 first seconds a tendency of mixture quality changes at the above mentioned ultrasound power, manifests itself: increase of acidity in the fresh mixture (fig. 1) starts decreasing and settles at a certain level. The level is determined by ultrasound intensity P: when P increases pH decreases – a larger well – balanced acidity is for a larger over cavitation P. Dynamics of the used mixture qualities varies – its acidity increases approaching a well balanced pH = 2÷3. In fact it is not affected by ultrasound intensity. Acidity settles in less than in 100 seconds. These index and ion concentration changes are interesting in view of kinetic energy and chemical processes. According to the ion kinetic equation, intensive ion generation during ultrasound cavitation is followed by a reverse process, i.e. ion recombination. When generation and recombination speed is the same equilibrium is settled. We have to include in the ion state equation the term dn′ of chemical reactions, which couses the change of ion quantity, so for the further study we have used the equation:

$$dn/dt = N - \alpha n^2 - dn',$$

here n – ion (negative and positive) concentration, N – generation power, α – recombination coefficient.

If we assume that generation speed in mixtures containing the same ingredients during the process of cavitation is more or less the same different moves of curves 1 and 2 can be conditioned by a different recombination speed: speed of case 1 is higher and that of case 2 is lower: besides, recombination speed in fresh mixture drops when ultrasound intensity increases (fig. 2, curve 1), while in the used mixture the speed of ion recombination, to all appearance, is not affected by ultrasound power.

Taking in to account that experimental data can be described theoretically by equations:

$$n = n_0 + A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}}$$

generation,

$$n = n_0 - A_3 e^{-\frac{t}{\tau_3}}$$

recombination, respectively, and the fact that pH index has a direct reference to the ion pair concentration the characteristic duration time (τ) of the processes has been determined.

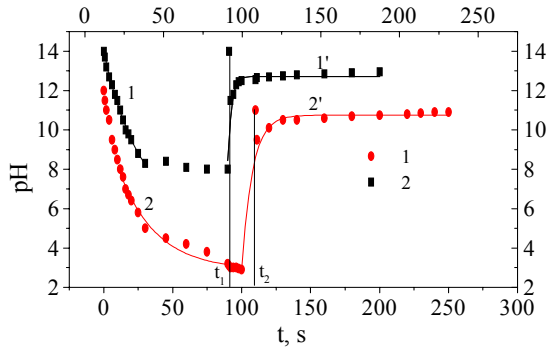

Fig. 2. **Dependency of mixture hydrogen potential pH on time t at a significant overcavitation ultrasound intensity W_2: 1 – for fresh mixture S5, 2 – for used mixture S2. The points – experimental data, linear the theoretically calculated.**

The data of theoretical calculation are presented in the table. As we can see from this table when the ultrasound radiation is turned off ion quantity rapidly decreases and the relaxation time in different cases is different. It has turned out that the recombination takes place more intensive in the case when the ultrasound intensity is much higher than the cavitation threshold and it has been against all expectations.

In the process of ion generation for the fresh mixture we have determined even two duration times of ion existence, which depend on the ultrasound intensity.

When the intensity P is in the minimal over cavitation level for the fresh mixture at the settling of equilibrium generation-recombination process some growth of recombination level with the duration time τ_{03} is observed (in time interval 25 – 100, s Fig. 1, curve 1). With increasing of the intensity P (Fig. 2, curve 1) this recombination growth disappears (in time interval 25–t_1, s).

The reasons for such behavior are determined by chemical changes and we found no data so far enabling us to give a more exhaustive description of such processes.

We have investigated instability of water mixture (with certain components) qualities caused by ultrasound radiation when ultrasound intensity is changed: evaluation of index pH has been performed in the fresh and in the used mixtures. Besides, pH saw changes when ultrasound was intensifical up to the point when

Table 1**. Duration times of generation and recombination processes for the different intensity P**

	for the minimal over cavitational ultrasound intensity			
	generation			recombination
	τ_1, s	τ_2, s	τ_{03}, s	τ_3, s
S5	9,43±0,16	87,12±0,21	16,49±0,45	25,07±1,63
S2	31,55±2,25	–	–	14,93±1,98
	for the intensity much higher then cavitation threshold			
	generation			recombination
	τ_1, s	τ_2, s	τ_{03}, s	τ_3, s
S5	18,35±0,16	34,35±0,22	–	2,69±0,23
S2	27,17±3,62	–	–	7,79±0,66

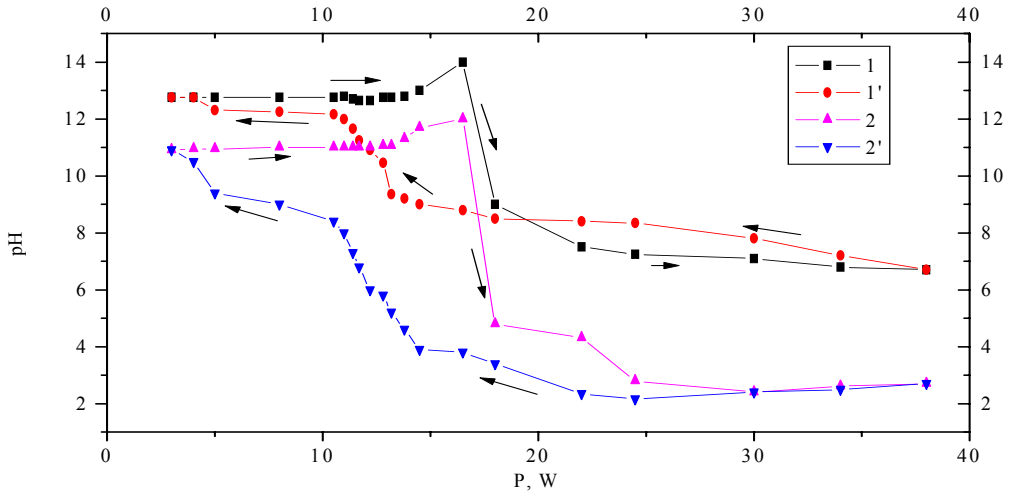

Fig. 3. **Dependency of mixture hydrogen potential pH on ultrasound power P: curves 1 and 1′ are for fresh mixture S5, 1 - by increasing P, 1′ - by decreasing P, curves 2 and 2′ for used mixture S2, 2 - by increasing P, 2′- by decreasing P.**

equilibrium is settled and ω was decreased till cavitation disappears and complete weakening of ultrasound power sets in. The obtained data are presented in fig. 3. As index pH at a definite ultrasound intensity relaxes in time, the presented data are obtained whenever equilibrium is reached. In fig. 3 curves 1 and 1′ represent fresh mixtures, 2 and 2′ – used mixtures. Data analysis showed that quality resistance to ultrasound effect in fresh mixtures is much higher than that in used mixtures: pH index changes are considerably smaller in the fresh mixture – from 13 to t, i.e. about 2 times, and of the used mixture about 5 times – from 11 to 2. Conclusion can be drawn, that mixture components in the latter sample have degraded and they behave like water that is by admixture [1].

Analyzing mixture behavior in view of ion concentration dynamics we could state that qualitative processes in both fresh and used mixture samples are analogous: in precavitation area the concentration of ions remains stable; when cavitation sets in, a decrease in ion number characteristic of all cases is observed – a slight alkalization of the mixture appears. With respect to ion conditions, extra ions generated during initial cavitation stimulate the process of recombination and ion number decreases; generation becomes very intensive, if increasing the ultrasound intensity is continued – the number of excited molecules gas up significantly, and the number of generation acts starts exceeding the number of recombination acts. Although the recombination number is determines by the square of ion concentration, the estimated data show that the process of recombination is nonlinear-recombination ratio a_1 represents the function of ultrasound intensity P: $a_1 = f(P)$. Without carrying out some special research it is difficult to say what kinds of process determine that. The data show that recombination is hardly possible at such ultrasound intensity ion equilibrium settles when there is in creased acidity. We investigated ion dynamics then the intensity of ultrasound was decreased, too, i.e. we observed ions returning from their excited state to the initial, unexcited one, and then passing on to precavitational area of intensity. Data of curves 1′ and 2′ show that neutralization process is different – the hysteresis of ion concentration is observed: if ultrasound intensity is decreased (curves 1′ and 2′), the intensity which needs to generate the same quantity of ions as in the ultrasound intensity increasing case is lower. Such kind of hysteresis is of interest, though new information on the mixture qualities is vague so far. Excited molecules become neutral – relaxation is observed at equilibrium number of ions, that is characteristic of both fresh and used mixtures. No changes were found at the initial stage. Data in figure 3 inform us that degradation of the cleaning mixture is mainly caused by its acidity: alkalization of the used mixture is decreased: from pH = 13 – for fresh mixture to pH = 11 – for used mixture. When the fresh mixture is used, alkalinity during a cleaning process remains close to neutral, pH ~ 8; the used mixture has lost all alkaline qualities, pH ~ 2÷4. These changes are determined by the change in chemical composition of the mixture that appears due to ultrasound radiation.

References

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Ultragarsinio plovimo mišinių senėjimas

Reziumė

Darbe lyginamos kai kurio šviežio ir naudoto plovimo mišinio savybės. Išmatuota, kaip keičiasi vandenilio potencialas šiuose mišinių bandiniuose priklausomai nuo ultragarsinės radiacijos trukmės ir ultragarso galios. Šviežiame ir naudotame mišinyje vandenilio potencialo rodiklio pte reikšmės gerokai skiriasi. Atkreipiamas dėmesys, kad jonų elektrokinetiniai procesai šiuose bandiniuose irgi yra labai skirtingi. Nustatyti jonų gyvavimo bei jų rekombinacijos būdingieji laikai. Daroma išvada, kad šviežias mišinys yra gerokai atsparesnis ultragarso poveikiui, tačiau po daugkartinio ultragarso poveikio mišinio savybės blogėja - jis sensta. Senėjimo priežastis yra jame vykstantys negrįžtami cheminiai procesai.