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**INFLUENCE OF ZETAG 63 SONICATION  
ON AGGREGATION AND BREAKAGE PROCESSES  
IN A TANK WITH TURBINE MIXER**

**WPLYW SONIFIKACJI WYBRANEGO FLOKULANTU  
NA PROCESY AGREGACJI I ROZPADU KREDY  
W ZBIORNIKU Z MIESZADŁEM TURBINOWYM**

**Abstract:** Flocculation process is commonly used in different industrial branches, eg in sewage sludge treatment. New methods are constantly developed for efficiency improvement or enhancement of other desirable end product features. It was proved that ultrasonic sonication of flocculant advantageously influences dewaterability parameters of sewage sludge. The final water content was decreased. Moreover, a half of dosage of the sonicated flocculant allowed one to achieve the electrokinetic potential equal to that achieved with a full dosage of the unmodified flocculant. An influence of ultrasonic sonication of the industrial flocculant ZETAG 63 on the particle size distribution of chalk suspension in distilled water is presented. Measurements were taken with the use of the laser particle size analyzer Frisch Analysette 22.

It was shown that sonication of flocculant had a negative impact on flocculation process and resulted with the decreased efficiency of polymer flocculating properties, ie the mean particle diameter decreased.

**Keywords:** aggregation, breakage, flocculation, ultrasounds, mixing

Aggregation process is commonly used in different industrial branches [1], eg in sewage sludge treatment. A typical goal is to enlarge a solid particle size in suspension for its easier removal. Then sludge is dewatered (eg via filtration), dried and utilized. As a flocculating agent different types of high-molecular weight cationic, anionic or nonionic polymers are used. When added to solid-liquid suspension they form branched flocks significantly larger than primary aggregates. This process runs in four steps [2]: mixing, adsorption of polymer on particle surface, reformation and finally flocculation via branching phenomenon. As an alternative to the mentioned process the charge neutralization or charge electrostatic patch mechanisms may appear. This process is called in general the aggregation. However aggregates are simultaneously broken due to

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shear forces resulting from turbulent flow in a mixer. These two opposite phenomena compete during the process leading after a certain period of time to a steady state. It can be described mathematically by the general aggregation-breakage equation [3]:

$$\begin{aligned} \frac{\partial n(v, t)}{\partial t} = & \frac{1}{2} \int_0^v \beta_{ag}(v-u, u) n(u, t) n(v-u, t) du + \int_v^\infty b(v, u) \beta_{br}(u) n(u, t) du + \dots \\ & \dots - \int_0^\infty \beta_{ag}(v, u) n(v, t) n(u, t) du - \beta_{br}(v) n(v, t) \end{aligned} \quad (1)$$

where: first two expressions on the right-hand side of Eq. (1) represent the birth terms due to the aggregation and breakage and last two expressions represent the death terms due to the aggregation and breakage.

There are many attempts to enhance flocculation process [4] or to adjust different parameters of end product, eg dewaterability characteristic. Among the others, there are application of electromagnetic field [5], flocculant blends [6] or polymer-surfactant mixtures as flocculating agents [7]. A practical application of ultrasonic field was considered since the beginning of the 20<sup>th</sup> century [8]. At present, it is used in many ways, eg in surface cleaning [9], crystallization or extraction [10]. Ultrasounds have also found application in air [11] and water cleaning [12]. In power plants ultrasonic field is used to sonificate flue gases, which leads to aggregation of solid particles [13]. This is usually initial process before an electrofilter unit. Its goal is to remove larger particles from the gas stream and to aggregate smaller ones which would not be stopped in an electrofilter. In water treatment facilities ultrasounds may be used in many ways [14–17]. Among others there are sludge disintegration [18] or ultrasonic conditioning of excessive deposit [19]. Wolny [20] researched an influence of ultrasonic field on sludge structure and its dewaterability properties. She proved that ultrasonic sonication of flocculant had a positive influence on many properties of flocculated sludge, eg final water content or a value of electrokinetic potential.

## Materials and measurement procedure

The experimental setup consisted of a mixing tank with the turbine, laser particle size analyzer Fritsch Analysette 22, peristaltic pump, ultrasonic horn and computer (Fig. 1).

In experiments the cylindrical mixing tank of a volume  $V_{zb} = 5.39 \cdot 10^{-3} \text{ m}^3$  equipped with 4 baffles was used. The tank of inner diameter  $D_{zb} = 0.19 \text{ m}$  was made of metaplex. The agitator (turbine) of diameter  $8 \cdot 10^{-2} \text{ m}$  was driven by the direct current engine Heidolph RZR 2102 control type (Heidolph Instruments GmbH). The turbine was placed  $6 \cdot 10^{-2} \text{ m}$  above the bottom of the tank. Suspension was drawn from the mixer by tubes and circulated in a closed system. After examination in the laser particle size analyzer the suspension came back to the tank. This experimental setup was based on the earlier research reports found in the literature [21, 22].

The ultrasonic horn VCX 130 by Sonics was used as a source of ultrasounds acting on flocculant. The horn was of 6 mm in diameter and length of 113 mm, made of

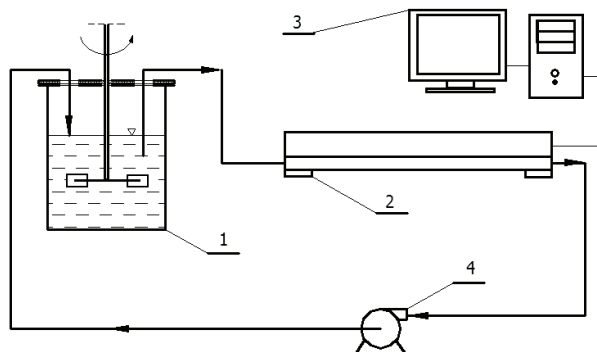


Fig. 1. Laboratory setup scheme: 1) mixing tank, 2) laser particle size analyzer, 3) computer, 4) peristaltic pump

titanium alloy TI-6AL-4V. It worked with the amplitude of 123  $\mu\text{m}$  and frequency of 20 kHz. The power supply was equal to 130 W. The experimental medium used was the suspension of commercial chalk ( $d_{32} \approx 2 \cdot 10^{-6}$  m) in distilled water. An amount of 1.5 g of chalk was weighted on the analytical balance and mixed with a small amount of distilled water. Such mixture was added to  $5.39 \cdot 10^{-3}$  m<sup>3</sup> (full mixing tank) of distilled water. Chalk was added while the agitator was working. The amount of chalk was chosen in a way to assure optimal working conditions for the laser particle size analyzer.

Zetag 63 is a synthetic, high-molecular weight cationic polyacrylamide of medium charge, used mainly in sewage treatment processes. An appropriate amount of dry solid ZETAG 63 was poured to a flask of volume 50 cm<sup>3</sup>, then 1.5 cm<sup>3</sup> of methanol was added to moisturize crystals and finally distilled water was added to achieve 0.1 % wt concentration of the solution. The flocculant was used 24 h after preparation. It was stored in a fridge at temperature about 5 °C, no longer than 4 days. Flocculant samples of a volume 10 cm<sup>3</sup> were sonificated in a glass beaker for different periods of time equal to 2, 4, 6, 8 and 10 seconds.

After addition of chalk (during mixing) to the mixing tank filled with distilled water a suitable measurement was taken (measurement zero). Then the flocculant was added (1.33 mg g<sup>-1</sup> of chalk) using a pipette and the stopwatch started. Each flocculant was examined without and with sonification. Measurements were taken after 1, 3, 5, 10, 15 and 20 minute and repeated at least three times to eliminate measurement errors. A rotational frequency of the mixing turbine was set to 200 rpm.

## Results and discussion

The dosage of 1.33 mg unmodified polymer per 1 g of chalk resulted in a significant enlargement of size of particles in suspension. A mean size of aggregates was about ten times greater in the end flocculation process (Fig. 2).

After the injection of polymer the particle size distribution (PSD) moved rapidly toward the high size classes. After the first minute the largest aggregates had a size

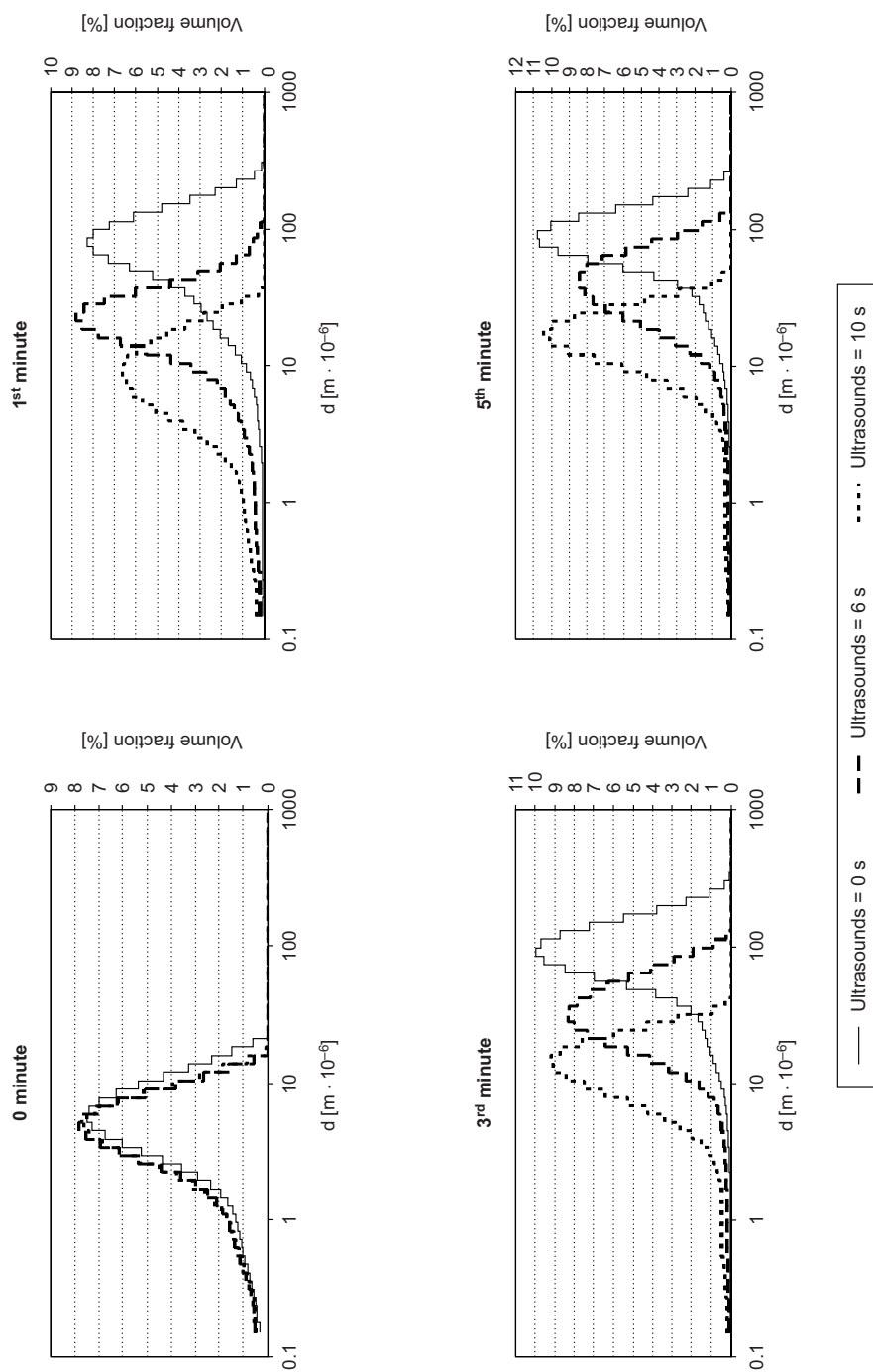


Fig. 2. The change of the particle size distribution during flocculation process for unmodified flocculant and sonicated for 6 and 10 seconds

above  $3 \cdot 10^{-4}$  m. In steady state the PSD was unimodal with a size of all aggregates smaller than  $2.5 \cdot 10^{-4}$  m. Although strong flocculating effect occurred, the lowest size class of  $0.16 \cdot 10^{-6}$  m was still present in the suspension. During the process a decrease of turbidity was observed. In a case of the modified flocculants, the PSD is also unimodal in the steady state. But the mean size of particles is smaller than in a case of the unmodified flocculant which could be also seen via a change of turbidity. With the usage of flocculant sonicated for 10 seconds there are no larger aggregates than  $50 \cdot 10^{-6}$  m in the suspension.

Ultrasonic sonication had a negative influence on flocculation process. In a case of ZETAG 63 the mean diameter of aggregates decreased with the time of sonication (Fig. 3). The largest changes were noticed during first six seconds of modification where  $d_{32}$ , ie volume to surface mean diameter, so called Sauter diameter, changed from  $20 \cdot 10^{-6}$  m to  $10 \cdot 10^{-6}$  m.

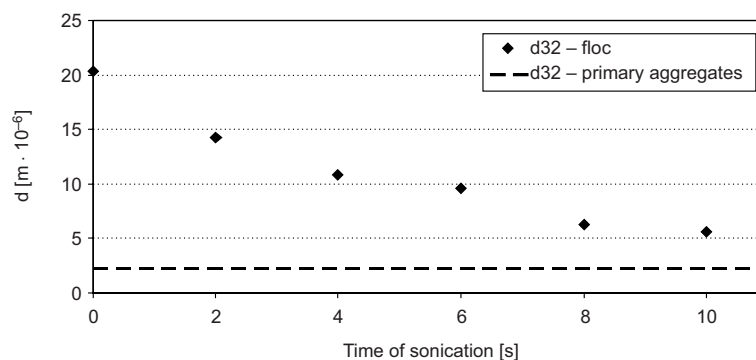


Fig. 3. Change of the Sauter mean diameter in the steady state vs time of sonication

Primary aggregates showed compact, oval structure (Fig. 4a). Flocks created with the unmodified flocculant were very branched and porous (Fig. 4b). They had a strongly developed 3D structure. During sonication the structure of polymer changed from long strongly branched chains to the short simple ones. This resulted with a change of flock structure – flocks became smaller and more compact (Fig. 4c).

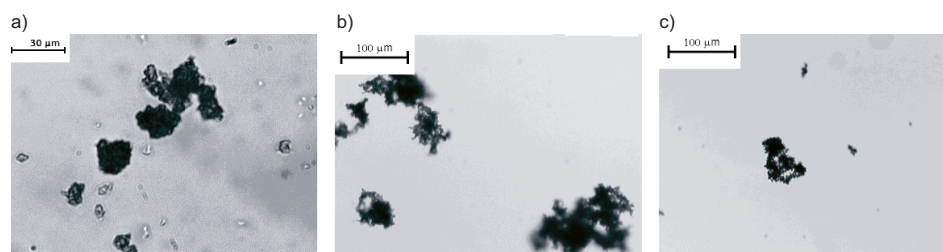


Fig. 4. Aggregates: a) before flocculation (primary aggregates), b) after flocculation with the unmodified flocculant, c) after flocculation with the flocculant sonicated for 6 seconds

## Conclusions

In tested ranges of parameters ultrasonic sonication of ZETAG 63 flocculant had a negative influence on flocculation process. A mean diameter of flocks decreased with sonification time. The largest changes were observed within two to six seconds of modification. The polymer sonicated for ten seconds showed almost no flocculating properties. There were no significant changes in a PSD shape.

The polymer underwent ultrasonic degradation resulting in mid-chain scission. Modification of flocculant resulted in modified structures of the created flocks. They were less porous and had the poorly developed 3D structure.

Although ultrasonic sonication made worse flocculation properties of the polymer, a change of structure of flock is crucial for dewaterability properties of sludge. Typically less porous aggregates contain less water. Also their surface is "smoother" which results in a better packing in sludge. Summing up, one can conclude that wider research is needed to define a more general influence of ultrasonic sonification on different types of flocculants.

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**WPLYW SONIFIKACJI WYBRANEGO FLOKULANTU NA PROCESY AGREGACJI  
I ROZPADU KREDY W ZBIORNIKU Z MIESZADŁEM TURBINOWYM**

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**Abstrakt:** Proces flokulacji jest powszechnie stosowany w różnych gałęziach przemysłu, m.in. w oczyszczalniach ścieków. Wciąż poszukuje się nowych metod zwiększenia jego efektywności czy też poprawy innych, pożądanych cech produktu końcowego. Udowodniono, że ultradźwiękowa sonifikacja flokulantów korzystnie wpływa na parametry odwadniania osadów ściekowych. Zmniejsza ona końcową zawartość wody. Ponadto, połowa dawki nadźwiękowanego flokulantu pozwala osiągnąć potencjał elektrokinetyczny równy potencjałowi w przypadku użycia pełnej dawki niemodyfikowanego flokulantu. W pracy przedstawiono wpływ ultradźwiękowej sonifikacji przemysłowego flokulantu ZETAG 63 na rozkład ziarnowy zawiesiny kredy w wodzie destylowanej. Badania przeprowadzono przy wykorzystaniu laserowego analizatora ziarnowego Analysette 22 firmy Fritsch.

Wykazano, że sonifikacja flokulantu ma niekorzystny wpływ na proces flokulacji i skutkuje osłabieniem możliwości flokujących polimeru, tj. średni rozmiar ziarna zmniejsza się.

**Słowa kluczowe:** agregacja, rozpad, flokulacja, ultradźwięki, mieszanie