Space-resolved sonochemistry in cleaning vessels in comparison to mechanical effects

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Introduction

There are many applications of ultrasound in medical science and engineering which are based on the physical effect of cavitation in liquid media such as cleaning and sonochemistry. Unfortunately, cavitation is a stochastic process and is strongly influenced by environmental conditions. This makes it difficult to control or even optimise a certain application process. Up to now, empirical assessment methods have been used to account for the influence of parameters such as temperature, frequency, vessel geometry, surfactants, input power and others, because an objective description of the different cavitation effects is lacking. Therefore, a project at PTB aims to relate different cavitation effects to each other and to measurement parameters obtained from the underlying sound field.

For this task, a measurement set-up for ultrasonic vessel investigation was extended by spatially resolved sonochemical measurement capability. This paper presents a direct comparison between measurements for sonochemical efficiency and the erosion effect in a standard ultrasonic vessel.

The basic vessel test facility

The ultrasonic vessel test facility combines different measurement methods required to determine the vessel's efficiencies corresponding to the different cavitation effects. Furthermore, several parameters describing the sound field are determined.

Sound field

The sound pressure in the filled vessel is determined using a standard hydrophone for the kHz range (e.g. B&K 8103). The sensor can be moved by a 3-axis controller for fast space-resolved measurement. The spectrum is analysed to yield the following parameters: amplitude of fundamental at excitation frequency f_0, amplitudes of subharmonic ($1/2\,f_0$), of ultraharmonic ($3/2\,f_0$) and of first harmonic ($2\,f_0$), and the average amplitudes of noise in low (100 kHz – 200 kHz) and high (1 MHz – 1.25 MHz) frequency range.

Erosion detection

For erosion measurements, standard aluminium foils of 20 µm to 30 µm thickness are used to be exposed in the vessel. The mechanical effect of cavitation, which is used for cleaning, leaves its mark on the foil as an erosion pattern. The insonated foil is scanned to form an electronic image by use of a tuned image scanner. Then, the electronic image can be analysed for three different kinds of bubble impacts:

- perforations, i.e. holes in the foil;
- ridges, i.e. ablation not succeeding in a hole;
- dents, which are bubble grooves without any material ablation.

Finally, the three impact types can be weighted individually and combined to form a quantitative erosion distribution graphic.

Sonochemistry detection

The sonochemical effect of cavitation mainly refers to the homolytic dissociation of the water molecule H_2O into a hydrogen atom H· and a hydroxyl radical OH·. Especially the latter is highly reactive and may convert to further reactive substances such as hydrogen peroxide H_2O_2. Moreover, dissociation might also happen to dissolved gas molecules such as oxygen O_2. This leads to the fact that reactions in aqueous solutions irradiated by ultrasound are difficult to describe in full [1]. Nevertheless, the purpose here is to find a measure for the sonochemical activity in ultrasonic vessels which is reliable and easy to use.

After testing several alternatives, potassium iodide was found to fit all our needs. Following [1], the key reactions are: Homolytic dissociation of water (1), oxidation of iodide ion I^- to iodine I_2 (2) and formation to the tri-iodide ion complex I_3^- (3).

$$H_2O \rightarrow H\cdot + OH\cdot \qquad \text{Dissociation} \qquad (1)$$

$$\begin{aligned} OH\cdot + I^- &\rightarrow OH^- + I \\ I + I^- &\rightarrow I_2^- \\ 2I_2^- &\rightarrow I_2 + 2I^- \end{aligned} \qquad \text{Oxidation} \qquad (2)$$

$$I^- + I_2 \rightarrow I_3^- \qquad \text{Complex formation} \qquad (3)$$

Finally, the production of tri-iodide ions I_3^- is used as a measure of the sonochemical activity.

Several preliminary investigations were performed on the tri-iodide dosimeter. So, the yield in I_3^- ions was proportional to the exposure time (linearity). Moreover, the starting solution, usually 0.5 molar KI, proved to be stable for several days if stored in the dark. So, measurements are not affected by the time period between insonation and analysis. The sensitivity of the dosimeter is sufficient to reach a typical signal-to-noise ratio of about 13 dB for irradiation durations of a few minutes in a standard ultrasonic vessel.

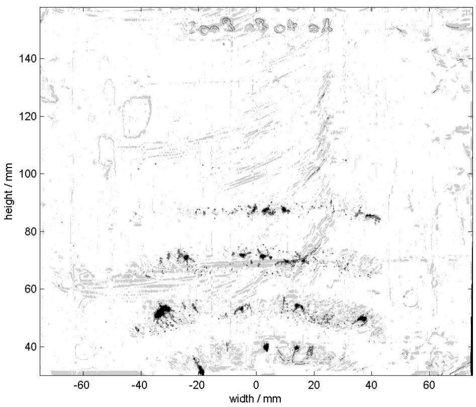

Figure 1: Final erosion distribution graphic of the insonated, scanned and analysed aluminium foil.

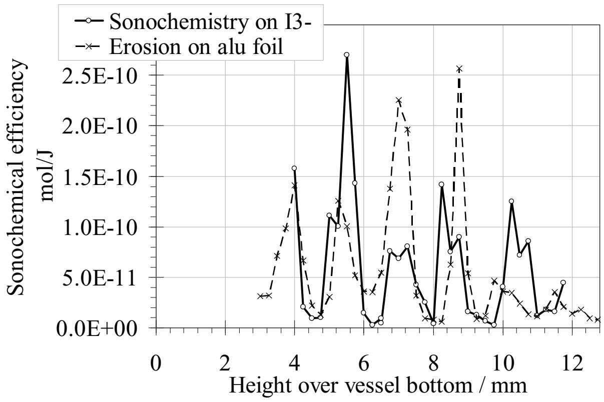

Figure 2: Sonochemical efficiency compared to erosion impact in an ultrasonic vessel measured in a straight line from the bottom of the vessel to the surface. The filling was deionised water saturated with air, and the filling level was 12.8 cm.

The measurement of the I_3^- ions' concentration is performed spectrometrically. The extinction spectrum shows two specific peaks for I_3^- at 288 nm and 352 nm. Since the huge number of I^- ions have strong extinction in the UV range, too, a complete band analysis must be performed to gain proper values for the extinction only caused by I_3^-. By using literature values for the molar extinction coefficient [2], the ion concentrations can be obtained by the extinction coefficient.

During exposition, the electrical active power to the ultrasonic transducers was monitored. This is equivalent to measuring the power input calorimetrically using the temperature increase which is the method usually applied in literature. The advantage of the electric power method is that input power can still be measured while keeping the vessel temperature constant by use of a thermostat.

Finally, the I_3^- concentration is normalised to the average electrical input power and to the exposure time. This leads to a quantity often called the sonochemical 'efficiency' as the number of ions produced per ultrasonic energy amount ([mol/J]). This can serve as a measure of the sonochemical cavitation effect.

It should be mentioned here, that the power normalisation described above neglects the transducer cavitation efficiency, i.e. the ratio of the electric power to the transducer which is present in the cavitation field. But since there is no measurement method for this coefficient known to the authors, the total power input to the transducer is the most reliable reference value for the power normalisation.

Since sound field measurement and erosion detection are spatially resolved, it would be desirable to determine local efficiency values for the sonochemistry detection, too. To restrict the reaction to a limited volume, small portions of the starting solution of about 2 ml were packed in samples. These consist of polyethylene (PE) foil of about 30 µm in thickness welded to small pads by hand using a bag sealer. This configuration allowed the isolation of a specific volume in the vessel with minimum disturbance of the cavitation activity.

Measurements

In a first experiment, about 20 pads filled with the starting solution were arranged back-to-back to determine the sonochemical efficiency along a straight line from the bottom of the vessel up to the surface. The samples were irradiated all at once and analysed as described above. Measurable I_3^- concentrations were only found in the lowest sample placed close to the transducer. All samples given above showed no sonochemical activity. This suggests a kind of shielding effect. The amount of pads all placed at once in the vessel strongly disturbs the cavitation field distribution compared to the empty vessel.

Consequently, the measurement was repeated but the samples were exposed one after another. The temperature was kept constant at about ±1°C and the electric input power was monitored and its average value used afterward for the normalisation of the tri-iodide ion concentrations. It also turned out to be essential to calm the surface motion, for instance by using a cover of PE film. A slow oscillation of the vessel filling started at certain filling levels, depending on the geometrical vessel characteristics which inhibit a stable cavitation field.

The measurement resulted in a pattern showing a standing wave with maxima and minima in the sonochemical efficiency, displayed as the straight line in Figure 2. The period of the wave matches half the wave length at the excitation frequency in the vessel of about 45 kHz, indicating that sonochemical efficiency is high in the antinodes and about zero in the nodes. A similar pattern was found in [3] but with a differing measurement set-up.

Whereas in practise usually a diffuse field is preferred in the vessel, the standing wave pattern found allows us to directly compare the spatially resolved sonochemical measurement to an erosion measurement.

The corresponding erosion distribution graphic of the aluminium foil treated as described above is shown in Figure 1. When comparing both cavitation effect measurements, one must be aware that the erosion graphic presents just a cross-sectional view of the volume covered by one sonochemical pad. The smaller the pad volume compared to the variations in the cavitation field structure, the more comparable are the measurements. Calculating the averaged erosion value of the cross-sectional area for all pads, the dashed curve in Figure 2 was found, and it shows good agreement with the sonochemical efficiency curve, especially for the locations of the minima and maxima. So, the final conclusion that can be drawn is that zones of high erosion capability are also zones of high sonochemical efficiency.

Conclusions

A test facility for ultrasonic vessels was set up, allowing not only sound field measurements and erosion detection but sonochemical measurements, too. Since all measurements are spatially resolved, measures of different cavitation effects can be compared to each other and to the sound field.

In the further course of the project, sonoluminescence detection shall be included in the facility as another cavitation effect. Moreover, series of measurements are planned to systematically vary environmental parameters and investigate correlations between the sound field and cavitation effects.

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