Dissertation

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Antti Grönroos

Ultrasonically Enhanced Disintegration

Polymers, Sludge, and Contaminated Soil

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VTT

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Abstract

There are a great variety of potential applications of high–intensity ultrasonic energy. Of these, cleaning, plastic pounding, and at present also sludge disintegration and the remediation of contaminated soil are probably the best known and offer the most general market for high-intensity ultrasonics. All developments within the area of ultrasound applications lead to the creation of environmentally friendly processes and compounds, emphasizing the role of ultrasound in "green chemistry". Ultrasound technology is considered not easy to use in industrial processes, since devices providing high sonic energy are not easy to construct. This thesis investigates on a semi-pilot scale if it is possible to enhance the disintegration of three quite different samples: polymers, sludge, and contaminated soil by using ultrasound.

The results indicate that it is possible to enhance the disintegration of polymers by means of ultrasonic power only when the cavitation threshold is exceeded. Above the cavitation threshold, the most extensive degradation took place at the lowest ultrasonic frequency used. The biggest decrease (from 115,000 g/mol to 30,000 g/mol) in relative molecular mass (RMM) was observed when the concentration of polyvinyl alcohol (PVA) was the lowest (1.0%). However, in the case of carboxymethylcellulose (CMC) it was observed that when viscosity was not adjusted there is an optimum polymer concentration (1.5–2.0%) where degradation is most efficient. The thesis shows that the extent of ultrasonic depolymerization decreases with decreasing molecular mass of the CMC polymer. The study also reveals that ultrasonic irradiation causes narrowing of the molecular mass distribution. The degradation of CMC polymer proceeded linearly and the rate of ultrasonic depolymerization decreased with decreasing molecular mass. In cases where the initial dynamic viscosities of polymer solutions were not the same, the sonolytic degradation of CMC polymer mainly depended on the initial dynamic viscosity. The higher the initial dynamic viscosity, the faster the degradation. This work confirms the general assumption

that the shear forces generated by the rapid motion of the solvent following cavitational collapse are responsible for the breakage of the chemical bonds within the polymer. The effect of polymer concentration could be interpreted in terms of the increase in viscosity with concentration, causing the molecules to become less mobile in solution with smaller velocity gradients around collapsing bubbles.

Ultrasonic disintegration of sludge increased the amount of soluble chemical oxygen demand (SCOD) and the production of methane. Multivariate data analysis suggested that ultrasonic power, sludge dry solids (DS), sludge temperature, and ultrasonic treatment time significantly affect sludge disintegration. It was also found that high ultrasound power together with a short treatment time is more efficient than low ultrasound power with a long treatment time. When using high ultrasound power, the ultrasound propagation is an important factor both in cavitation erosion prevention and reactor scale-up. Ultrasound efficiency rose linearly with input power in sludge at small distances from the transducer. On the other hand, ultrasound efficiency started even to decrease with input power at long distances from the transducer. When using oxidizing agents together with ultrasonic disintegration there was no increase in SCOD and only a slight increase in total organic carbon (TOC) compared to ultrasonic treatment alone. However, when using oxidizing agents together with ultrasound, no enhancement in methane production was observed.

Ultrasound improved the remediation results of both products (sink and float products) in heavy medium separation. This phenomenom was based on the fact that the amount of ultrafine metal fraction was diminished when attrition conditioning was replaced by ultrasound. The remediation process produced float product (cleaned soil) that could be left where it was. This would make for lower process costs since there is no need to move large quantities of soil material.

Doctoral thesis

University of Jyväskylä, Department of Chemistry, Laboratories of Applied and Organic Chemistry, Jyväskylä, 2010

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Preface

This study was carried out in the Laboratories of Applied and Organic Chemistry at University of Jyväskylä. The experimental part of the work was carried out mainly during 1999–2006 at the Technical Research Centre of Finland (VTT), Jyväskylä.

First of all, I wish to express my sincere gratitude to Professors Raimo Alén and Erkki Kolehmainen of the University of Jyväskylä for their support and guidance during this work.

I am very grateful to VTT for giving me the opportunity to do this long-term work. I want to thank my colleagues at VTT for their great help, especially with my technical problems. I wish to express my special thanks to Dr. Tech. Hanna Kyllönen and Lic. Tech. Pentti Pirkonen for their support, encouragement, and valuable comments throughout my research work. The experimental part of the work was partly performed with the assistance of Hannu Sekki, Jorma Ihalainen, and Hannu Mursunen. I want to express sincere thanks to all of them.

I want to express my special thanks to my official pre-examiners, Professor José González García, Universidad de Alicante, and Professor Gareth J. Price, University of Bath.

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Finally, I want to thank Hanna and my whole family for their patience and support in every field during this work.

Jyväskylä, April 2010

Antti Grönroos

Contents

Appendices

Publications I–V

List of publications

This doctoral thesis is based on the following articles, which will be referred to in the text by the Roman numerals given below:

I	Grönroos, A., Pirkonen, P., Heikkinen, J., Ihalainen, J., Mursunen, H., and Sekki H., Ultrasonic depolymerization of aqueous polyvinyl alcohol, *Ultrasonics Sonochemistry*, Vol. 8, Issue 3, July 2001, pages 259–264.
II	Grönroos, A., Pirkonen, P., and Ruppert, O., Ultrasonic depolymerization of aqueous carboxymethylcellulose, *Ultrasonics Sonochemistry*, Vol. 11, Issue 1, January 2004, pages 9–12.
III	Grönroos, A., Pirkonen, P., and Kyllönen, H., Ultrasonic degradation of aqueous carboxymethylcellulose: Effect of viscosity, molecular mass, and concentration, *Ultrasonics Sonochemistry*, Vol. 15, Issue 4, April 2008, pages 644–648.
IV	Grönroos, A., Kyllönen, H., Korpijärvi, K., Pirkonen, P., Paavola, T., Jokela, J., and Rintala J., Ultrasound assisted method to increase soluble chemical oxygen demand (SCOD) of sewage sludge for digestion, *Ultrasonics Sonochemistry*, Vol. 12, Issues 1–2, January 2005, pages 115–120.
V	Kyllönen, H., Pirkonen, P., Hintikka, V., Parvinen, P., Grönroos, A., and Sekki, H., Ultrasonically aided mineral processing technique for remediation of soil contaminated by heavy metals, *Ultrasonics Sonochemistry,* Vol. 11, Issues 3–4, May 2004, pages 211–216.

The author Antti Grönroos was the main researcher and the author of articles I–III. In article IV Antti Grönroos was the author and the researcher in the areas of design of the ultrasonic reactors and propagation of ultrasound in the sludge studies. In article V the author Antti Grönroos was the researcher in the areas of ultrasonic reactor design and some ultrasound studies. Some of the measurements were done by technicians at VTT, the University of Jyväskylä, and GTK.

List of symbols

A	area	(m^2)
c	concentration	(mol/l)
c	velocity of sound	(m/s)
dx	thickness	(m)
E	energy density	(J)
E_t	energy of whole wave	(J)
f	frequency	(1/s)
I	intensity of acoustic field	(W/cm^2)
K_E	kinetic energy	(J)
m	mass	(kg)
M_{lim}	limiting value below which no further degradation takes place	(g/mol)
p	pressure of sound	(atm)
P	total pressure	(atm)
P_A	pressure amplitude	(atm)
P_a	acoustic pressure	(atm)
P_c	negative pressure on rarefaction	(atm)
P_h	hydrostatic pressure	(atm)
P_m	pressure at the start of collapse	(atm)

P_{max}	maximum pressure effects resulting from the cavitation bubbles collapse	(atm)
P_v	vapour pressure of the medium	(atm)
R	critical molecular distance	(m)
t	time	(s)
T_{max}	maximum temperature effects resulting from the cavitation bubbles collapse	(^{o}C)
U_0	the value of voltage	(V)
U_{eff}	the effective value of voltage	(V)
$U_{hydrofone}$	the hydrophone value of the voltage	(V)
v	velocity of layer	(m/s)
v_{max}	maximum velocity of the particle	(m/s)
v_p	velocity of the particles	(M/s)
v_s	velocity of sound	(m/s)
x	thickness of the layer	(m)
Y	phase difference of pressure amplitude and the velocity of an imaginary particle	(°)
z	acoustic impedance	(kg/m^{2}s)
λ	wavelength	(m)
ŋ	viscosity	(poise)
ρ	density	(g/cm^3)
σ	surface tension	(N/m)

List of abbreviations

BDH	British Drug House
BOD	biochemical oxygen demand
CMC	carboxymethylcellulose
COD	chemical oxygen demand
dc	direct current
DDT	4,4'-(2,2,2-trichloroethane-1,1-diyl)bis(chlorobenzene)
DNA	deoxyribonucleic acid
DS	dry solids
ENI	Electronic Navigation Industries
EPS	extracellular polymeric substances
GC-MS	gas chromatography-mass spectrometry
GTK	Geological Survey of Finland
HRT	hydraulic retention time
IEC	International Electric Co.
KAX	K-amyl xanthate
MM	molecular mass
NA	not analyzed
NaIPX	Na-isopropyl xanthate
NS	no significant meaning

PAH	polycyclic aromatic hydrocarbons
PCB	polychlorinated biphenyl
P.E.	population equivalent
PEG	polyethylene glycol
PLS	partial least squares
PVA	polyvinyl alcohol
RaRa	turnip fatty acid
RMM	relative molecular mass
SCOD	soluble chemical oxygen demand
SFS	Finnish Standards Association
SIF	separation in froth
SRT	sludge residence time
TCOD	total chemical oxygen demand
TOC	total organic carbon
TS	total solids
TVFA	total volatile fatty acids
US	ultrasonic
USA	United States of America
VS	volatile solids
VTT	Technical Research Centre of Finland
WAS	waste activated sludge
XRF	X-ray fluorescence

1. Introduction

The term “ultrasound” means vibrations which are similar to sound waves, but with frequencies too high to be detected by the human ear. The upper frequency limit of human hearing varies from about 10 kHz to about 18 kHz (Cracknell 1980). For any given person the threshold frequency decreases with increasing age. The basis for the present-day generation of ultrasound was established as far back as 1880 with the discovery of the piezoelectric effect and its inverse by the Curies. The first commercial applications of ultrasound appeared 1917 with Langevin’s echo-sounding technique for estimating the depth of water. Langevin’s discovery was the direct result of an idea which arose from a competition organized in 1912 to find a method to detect icebergs in the open sea and so avoid any repetition of the disaster which befell the Titanic. Cracknell (1980) reported that some work on the development of using ultrasonic cleaning was performed in Germany during the Second World War. Since that time ultrasonic cleaning equipment has been developed by many different manufactures for a wide variety of applications. For example, Mason and Lorimer (1988) reported 20 years ago that much of the ultrasonic equipment in industry is involved in welding or riveting plastic mouldings for the consumer market. Most modern ultrasonic devices rely on transducers which use the inverse effect, *i.e.* the production of a charge in the dimension of certain materials by the application of an electrical potential across opposite faces. If the potential is alternated at high frequencies the crystal converts the electrical to mechanical (sound) vibration – rather like a loudspeaker. At sufficiently high alternating potential, ultrasound is generated (Mason and Lorimer 1988).

There are a great variety of high-intensity applications and potential applications of ultrasonic energy (Mason and Lorimer 1988). They include cleaning, soldering, plastic pounding, spot welding of metals, liquid atomization, materials forming, foam control, emulsification of liquids, drying and dewatering, sludge disintegration, compaction of powered metals and plastic, acceleration of chemical activity, accelerated diffusion, alleviation of frictional effects, depolymerization, fragmentation and dispersion of particles, control of grain size in solidifying melts, dust and smoke precipitation, and many others. Of these, cleaning, plastic pounding, and also sludge disintegration and the remediation of contamined soil are probably the best known and offer the most general market for high-intensity ultrasonics. Even if really large-scale applications are still in the future, experiments starting from several tens of grams have already been reported (Kardos and Luche 2001). Recent progress in sonochemical engineering and in ultrasound generators with improved energetic yields should be applicable to industrialization. All these developments will lead to the creation of environmentally friendly processes and compounds, emphasizing the role of ultrasound in “green chemistry”. Ultrasound technology is considered not easy to use in industrial processes, since devices providing high sonic energy are not easy to manufacture. However, based on research work already carried out and referred to in this work there are industrial processes, where is used low energy ultrasound. For example, installing an ultrasonic device before an anaerobic unit consumes electricity produces no additional harmful matter, but greatly improves anaerobic efficiency. For this reason, ultrasonic technology may be a clean and “green” way to deal with sludge.

This study, first reviews general aspects of ultrasound, such as ultrasound generation, cavitation, and factors affecting cavitation. In this part there is also a discussion of the factors that have an effect on ultrasound-assisted polymer degradation, sludge disintegration or soil remediation. This is because the aim of the experimental part of this study was to investigate on a semi-pilot scale whether it is possible to enhance by ultrasound the disintegration of three quite different samples: polymers, sludge, and contaminated soil.

2. Aims of the study

The aim of the study was to investigate whether it is possible to enhance the disintegration process using ultrasound. For this purpose, three rather different samples (polymers, sludge, and contaminated soil) were studied in the laboratory on a semi-pilot scale.

3. General aspects of ultrasound

3.1 Introduction

This chapter is mainly based on the comprehensive books by Cracknell (1980), Ensminger (1988), Mason and Lorimer (1988), Suslick (1988), Mason (1991a), and Abramov (1998). Being a sound wave, ultrasound is transmitted through any substance, solid, liquid, or gas which possesses elastic properties (Mason and Lorimer 1988). The movement of the vibrating sound source is communicated to the molecules of the medium, each of which transmits the motion to an adjacent molecule before returning to approximately its original position. For liquids and gases, particle oscillation takes place in the direction of the wave and produces longitudinal waves (Figure 1 (a)). Solids, however, since they possess shear elasticity, can also support tangential stresses, giving rise to transverse waves, in which particle movement takes place perpendicular to the direction of the wave (Figure 1 (b)).

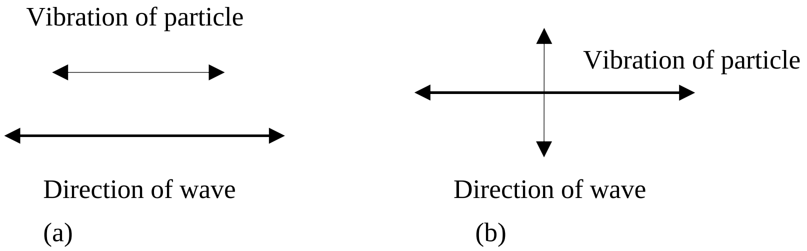


Figure 1. Wave and particle movement (Mason and Lorimer 1988): a) longitudinal waves and b) transverse waves.

The focus in this work was on the applications of an ultrasound in the liquid state and this medium was used in all experiments.

3.2 The generation of ultrasound – transducers

A transducer is the name for a device capable of converting one form of energy into another, a simple example being a loudspeaker which converts electrical energy to sound energy (Mason 1991a). Ultrasonic transducers are designed to convert either mechanical or electrical energy into high-frequency sound. There are three main types of ultrasound transducers: gas-driven, liquid-driven, and electromechanical equipment. The two main types of electromechanical transducers are based on either the piezoelectric or the magnetostrictive effect. The most commonly used are piezoelectric transducers and because these were also used in this thesis, they are more exhaustively described.

Piezoelectric materials have the following two complementary properties (Mason 1991a):

a) The direct effect – when pressure is applied across the large surfaces of the section, a charge is generated on each face equal in size but of the opposite sign. This polarity is reversed if tension is applied across the surfaces.

b) The inverse effect – if a charge is applied to one face of the section and an equal but opposite charge to the other face, then the whole section of crystal will either expand or contract depending on the polarity of the applied charges.

When applying rapidly reversing charges to a piezoelectric material, fluctuations in dimensions will be produced (Mason 1991a). This effect can be harnessed to transmit ultrasonic vibrations from the crystal section through the medium it is in contact with. Three materials (barium titanate, lead mataniobate, and the mixed crystal lead zirconate titanate) are commonly used as piezoelectric materials. These materials cannot be obtained as large single crystals and so, instead, they are ground with binders and sintered under pressure at above 1000 °C to form a ceramic. The crystallites of the ceramic are then aligned by cooling from above the ferroelectric transition temperature in a magnetic field. Ferroelectric ceramic materials are made piezoelectric by a biasing or polarization procedure. The procedure includes elevating the temperature of the material to above the Curie point and allowing it to cool slowly in a high dc electric field which is oriented along an axis of planned piezoelectric excitation. The Curie point is the temperature above which a material becomes inactive again (Ensminger 1988). It is not possible to use a given piece of piezoelectric material efficiently at every frequency. Optimum performance will only be obtained at the natural resonance frequency of the particular sample, and this depends upon its dimensions. This is why conventional ultrasonic equipment is of fixed frequency and why reports of comparative studies at different frequencies are not common (Mason 1991a).

To reinforce the rather fragile ceramic transducers it is normal practice to clamp piezoelectric elements between metal blocks, which serve both to protect the dedicated crystalline material and to prevent it from overheating by acting as a heat sink (Mason 1991a). Usually two elements are combined so that their overall mechanical motion is additive. The construction of such transducers is shown in Figure 2.

Figure 2. Piezoceramic ultrasonic transducers (http://safin0522.en.ec21.com/).

The sound wave is usually introduced to the medium by an ultrasonic bath, an ultrasonic bar or an ultrasonic horn (Mason and Lorimer 1988). In every case, an alternating electrical field (generally in the range 20–50 kHz) produces a mechanical vibration in a transducer, which in turn causes vibration of the bottom of the bath (or the probe) at the applied electric field frequency.

3.3 Cavitation bubble formation

The progression of a sound wave through a liquid medium causes the molecules to oscillate around their mean position (Mason and Lorimer 1988, Mason

1991a). During the compression cycle, the average distance between the molecules decreases, whilst during rarefaction the distance increases. If a sufficiently large negative pressure on rarefaction (P_c) is applied to the liquid such that the average distance between the molecules exceeds the critical molecular distance (R) necessary to hold the liquid intact, the liquid will break down and voids or cavities will be created and cavitation bubbles will be formed. Once produced, these cavities, voids, or bubbles may grow in size until the maximum of the negative pressure has been reached. However, in the succeeding compression cycle of the wave, they will be forced to contract, *i.e.* decrease in volume and some of them may even disappear totally. At the extreme of the rarefaction half of the cycle the bubble is at its maximum size and at the extreme of the compression half of the cycle it is at its minimum size.

It is possible to show that if the excess pressure amplitude of the ultrasound is sufficiently high, in other words if the intensity of the ultrasound is sufficiently high, and the initial size of the bubble is less than a certain critical value, the bubble will suddenly collapse during the compressional half of the cycle with the sudden release of a comparatively large amount of energy (Cracknell 1980). This collapse and the associated release of energy are known as cavitation. The pressure in a bubble just before it finally collapses may be very large indeed. Thus, when the bubble finally collapses an extremely powerful shock wave is produced and it is the energy in this shock wave which is responsible for many of the effects arising from cavitation. The shock waves produced on the total collapse of a bubble have been estimated to be of the order of several thousands of atmospheres and this is thought to be the cause of the considerable erosion of components observed in the vicinity of the bubble.

For any bubble created early in the rarefaction cycle, or initially present in the liquid, a growth in size will occur during the remainder of the cycle (Mason and Lorimer 1988). During the compression cycle all bubbles will be made to contract or collapse. However, if gas or vapor has diffused into the void or bubble during growth, complete collapse may not occur and the bubble may in fact oscillate in the applied field. Therefore, two types of bubbles must be considered: those which collapse completely (transient cavitation) and those which oscillate and exist for some considerable period of time (stable cavitation). Whether they collapse or oscillate depends upon many factors, *e.g.* temperature, acoustic amplitude, frequency, external pressure, bubble size, and gas type and content. There is further complication in that transient bubbles may grow into stable bubbles and *vice versa*. In any case it is certain that compression of a bubble containing either gas or vapor occurs very rapidly and leads to enormous temperatures (~10,000 K) and pressures (~1,000 atm) within the bubble itself. If complete collapse occurs, these pressures must be released into the liquid as shock waves.

During compression and rarefaction there will probably be several types of bubbles in the liquid, because during these cycles liquid vapor may, for example, evaporate into the partial void. Those bubble types may be (Mason and Lorimer 1988):

(a) the empty bubble (true cavitation),
(b) the vapor-filled bubble,
(c) the gas-filled bubble (unless the liquid is totally degassed), and
(d) a combination of vapor- and gas-filled bubbles.

3.3.1 Transient cavitation

Transient cavitation bubbles are voids, or vapor-filled bubbles, believed to be produced using ultrasound intensities in excess of 10 W/cm^2 (Mason and Lorimer 1988). They exist for one, or at most a few acoustic cycles, expanding to a radius of at least twice their initial size, before collapsing violently on compression, often disintegrating into smaller bubbles. These smaller bubbles may act as nuclei for further bubbles, or if of sufficiently small radius they can simply dissolve into the bulk of the solution. During the lifetime of the transient bubble it is assumed that there is no time for any mass flow, by diffusion of gas, into or out of the bubble, whereas evaporation and condensation of liquid is assumed to take place freely. If there is no gas to cushion the implosion a very violent collapse will result.

3.3.2 Stable cavitation

Stable bubbles are thought to contain mainly gas and some vapor and are believed to be produced at fairly low intensities (in water 1–3 W/cm^2), oscillating often non-linearly about some equilibrium size for many acoustic cycles (Mason and Lorimer 1988). The time scale over which stable bubbles exist is sufficiently long for mass diffusion of gas, and thermal diffusion, with consequent evaporation and condensation of the vapor, can occur, resulting in significant long-term effects. If the rates of mass transfer across the gas-liquid interface are not equal, this may result in bubble growth. In the rarefaction cycle gas diffuses from the liquid into the bubble, while in the compression cycle gas diffuses out of the bubble into the liquid. Since the interfacial area is greater in the rarefaction cycle, the inward diffusion is greater and leads to an overall growth of the bubble. As the bubble grows the acoustic and environmental conditions of the medium will change and the bubble may be transformed into a transient bubble and undergo collapse. The violence of collapse, however, will be less than that for a vapor-filled transient bubble since gas will cushion the implosion. On the other hand, the bubbles may continue to grow during subsequent cycles until they are sufficiently buoyant to float to the surface and be expelled.

3.4 Factors affecting cavitation

3.4.1 Frequency of ultrasound

To completely rupture a liquid and hence provide a void, which may subsequently become filled with gas or vapour, requires a finite time (Mason and Lorimer 1988). For ultrasound waves with high frequencies, the time required to create the bubble may be longer than the available time during rarefaction. Thus it may be anticipated that as frequency increases the production of cavitation bubbles becomes more difficult to achieve in the available time and that greater pressure amplitudes will need to be employed to ensure that the cohesive forces of the liquid are overcome. In fact, in earlier studies (Mason and Lorimer 1988) it has been found that ten times more power is required to make water cavitate at 400 kHz than at 10 kHz. Although various proposals have been offered to explain this observation, at least in qualitative terms it may be argued that at very high frequency, where the rarefaction cycles are very short, the finite time required for the rarefaction cycle is too small to permit a bubble to grow to a size sufficient to cause disruption of the liquid. Even if a bubble were to be produced during rarefaction the time required to collapse that bubble may be longer than that available in the compression half-time. The resultant cavitational effects will therefore be less at higher frequencies.

3.4.2 Intensity of ultrasound

The intensity of ultrasound is a very important factor when studying the effect of ultrasound on disintegration. Mason and Lorimer (1988) have reported that the molecules of the liquid, under the action of the applied field, will vibrate around their mean position. An acoustic pressure (P_a) will be superimposed upon the already ambient pressure (usually hydrostatic, P_h) present in the liquid. The total pressure (P) in the liquid at any time (t) is

$$P = P_h + P_a = P_h + P_A \sin 2\pi ft, \qquad (1)$$

where P_A is the pressure amplitude, f frequency, and t time.

For the ultrasound, as for any sound wave, the wavelength (λ) of sound in the medium is given by the relationship

$$v_s = \lambda f, \qquad (2)$$

where v_s is the velocity of sound in the medium and f frequency.

If the movement of a layer of the medium of area (A) and thickness (dx) under the action of the ultrasound wave are considered, the kinetic energy (K_E) of the layer is given by

$$K_E = ½\, mv^2 = ½\, (\rho Adx)v^2, \qquad (3)$$

where m is the mass of the layer, v the velocity of the layer, and ρ the density of the layer.

The energy of the whole wave (E_t) is obtained by summing all such elements, *i.e.* integrating equation (3) to give

$$E_t = ½\, \rho Axv^2, \qquad (4)$$

where ρ is the density of the layer, A the area of the layer, x the thickness of the layer, and v the velocity of the layer.

The energy per unit volume or energy density (E) is given by

$$E = ½\, \rho v^2, \qquad (5)$$

where ρ is the density of the layer and v the velocity of the layer.

If the sound energy passes through a unit cross-section area (A = 1) with a velocity of v_s, then the volume swept out in a unit time is v_s (since A = 1), and the energy flowing in a unit time is given by E v_s. Because intensity (I) has been defined as the amount of energy flowing per unit area per unit time

$$I = E\, v_s, \qquad (6)$$

where E is the energy intensity and v_s the velocity of sound.

Then we can obtain

$$I = ½\, \rho v_p^2\, v_s \qquad (7)$$

For a plane progressive wave, the particle velocity (v_p) can be shown to be related to the acoustic pressure (P_a) by the expression

$$P_a/v_p = \rho v_s \tag{8}$$

For maximum particle velocity (v_{max}) the amplitude of the oscillating acoustic pressure (P_A) is given by

$$P_A/v_{max} = \rho v_s, \tag{9}$$

i.e.

$$v_{max} = P_A/\rho v_s \tag{10}$$

Thus, the intensity of the sound wave (from equations (7) and (10)) can be expressed as,

$$I = ½ \rho v_{max}^2 v_s = ½ \rho (P_A/\rho v_s)^2 v_s = P_A^2/\rho v_s, \tag{11}$$

i.e. the sound intensity is proportional to the square of the acoustic amplitude.

In order to measure the sound intensity at a particular point in a medium, either the maximum particle velocity (v_{max}) or the maximum pressure amplitude (P_A) must be clearly determined. In practice, this is extremely difficult and for most ultrasonic applications a calorimetric determination of the total ultrasonic energy delivered to the medium is considered to be sufficient (Mason *et al.* 2004). Unfortunately, in ultrasound scale-up these calorimetric determinations are impossible to perform and so different kinds of intensity measurements are needed. In scale-up the ultrasonic intensity can be determined simply from the input or output power of the transducer per unit area of the transducer surface or using a hydrophone.

The intensity of ultrasound (I) relates directly to the amplitude of vibration of the ultrasonic source. In the strictest sense the ultrasonic intensity is the amount of energy carried per second per unit area by the wave (Mason and Lorimer 1988). The usual unit of ultrasonic intensity is W/cm^2. In general, an increase in intensity will provide for an increase in the cavitational effects. Cavitation bubbles, initially difficult to create, will now be possible. However, ultrasonic energy input to the system cannot be increased indefinitely for three reasons (Mason 1991a):

1. The transducer used in the sonicator will eventually break down as the increasing dimensional changes in the transducer eventually fracture the material.

2. At high vibration amplitude the source of ultrasound cannot maintain contact with the liquid throughout the complete cycle. This is technically known as decoupling and results in a great loss efficiency of transfer power from the source to the medium.
3. When a large amount of ultrasonic power enters a system a great number of cavitation bubbles are generated in the solution. Many of these will coalesce, forming larger and more stable bubbles. These may dampen the passage of sound energy through the liquid and also remove many of the smaller bubbles which would have collapsed to give ultrasonic effects.

The ultrasonic intensity is the amount of energy carried per second per unit area by the wave (W/cm^2). The power intensity can be determined simply from the input or output power of the sonicator per unit area of the transducer surface, calorimetrically or using a hydrophone. In this work the ultrasound power intensity was calculated using a hydrophone or by measuring the input power values, transducer surfaces, and the volumes of the reactors.

There are many types of acoustic probe that can be used to measure the pressure amplitude in the system (Berlan and Mason, 1996). In principle, the local acoustic power can be obtained by measuring the pressure amplitude (P) and the velocity (v_p) of an imaginary particle submitted to the field, and their phase difference (Y). Transmitted power can then be obtained by integrating $Pv_p\cos Y$ over the total volume. This is a good method for local measurements, but rather tedious for overall power. Furthermore, particle velocity has to be measured in order to calculate the ultrasonic power and this is not a trivial task. As an assumption, particle velocity may be assumed to be the same in the liquid and at the tip of the probe. Although this is almost never exactly true, this hypothesis can lead to a reasonable estimate of the dissipated ultrasonic power. For this reason, acoustic probes are widely used to calibrate ultrasonic equipment.

Acoustic impedance (z) is the relationship between sound power (p) and particle velocity (v_p). The acoustic impedance of a planewave is

$$z = p/v_p = \rho c, \qquad (12)$$

where ρ is the density of the medium and c is the velocity of sound in the medium.

One measure of the power magnitude of a sound wave is the acoustic intensity of sound. The acoustic intensity indicates the sound power which hits a particular surface (W/cm^2). Acoustic intensity has only a limited practical meaning because it is impossible to measure its magnitude directly. Nevertheless, acoustic intensity is a very useful quantity when determining ultrasonic power. In the case of vertical sonication of a surface, acoustic intensity (I) is determined by:

$$I = p^2/z, \qquad (13)$$

where p is the power of the sound and z the acoustic impedance of the medium.

The effective value of voltage (U_{eff}) is often defined by

$$U_{eff} = (\sqrt{2}/2)U_0 \qquad (14)$$

so

$$U_{eff} = U_0/\sqrt{2}, \qquad (15)$$

where U_0 is the value of voltage.

A hydrophone measures the power of sound as the voltage from peak to peak. Thus the hydrophone value of the voltage ($U_{hydrophone}$) has to be divided by 2 and so the effective value of the voltage is

$$U_{eff} = U_{hydrophone}/2\sqrt{2} \qquad (16)$$

The voltage efficiency of the hydrophone is a value which depends on the specification of each hydrophone and this must be noted in a sound power measurement. The voltage efficiency of the hydrophone is mentioned in the calibration papers of each hydrophone. Once the effective voltage and the voltage efficiency of the hydrophone are known, it is possible to calculate the power of sound which meets the hydrophone's square surface area:

$$p = U_{eff}/\text{voltage efficiency of the hydrophone} \qquad (17)$$

By measuring the power of sound using a hydrophone at different points within a reactor and using equations (14), (15), (16), and (17), it is possible to calculate the acoustic intensity of ultrasound (Borenius *et al.* 1981).

3.4.3 Solvent

Since it is necessary for the negative pressure in the rarefaction cycle to overcome the natural cohesion forces acting in the liquid, any increase in these forces will increase the threshold of cavitation, *i.e.* the point at which cavitation begins (Mason and Lorimer 1988). Therefore cavitation ought to be more difficult to produce in viscous liquids, or liquids with high surface tensions, or at low vapor pressure, where the forces are stronger and ultrasound waves with greater pressure amplitude (P_A) and hence greater intensity will be necessary. Once a liquid produces cavitation bubbles, however, the maximum temperature (T_{max}) and maximum pressure (P_{max}) effects resulting from collapse of the bubbles will be greater, since the pressure at the start of collapse (P_m) will have been larger. Table 1 shows, for example, the influence of viscosity, density, and sound velocity on P_A at which cavitation begins in several liquids at 25 °C at a hydrostatic pressure of 1 atm.

Table 1. The pressure amplitude (P_A) at which cavitation begins in several liquids at 25 °C at a hydrostatic pressure of 1 atm (Mason and Lorimer 1988).

Liquid	**ŋ, poise**	**ρ, g/cm^3**	**c, km/s^{-1}**	**P_A, atm**
Castrol oil	6.3	0.969	1.477	3.9
Olive oil	0.84	0.912	1.431	3.61
Corn oil	0.63	0.914	1.463	3.05
Linseed oil	0.38	0.921	1.468	2.36
CCl_4	0.01	1.60	0.926	1.75

As can be seen form Table 1, the influence of viscosity (ŋ) is more important for the cavitation threshold than the influence of density (ρ) or sound velocity (c).

3.4.4 Temperature

The temperature is known to affect the cavitation threshold. In general, the threshold limit has been found to increase with a decrease in temperature. For this reason, increasing the temperature allows cavitation to be achieved at lower acoustic intensity. This may be due in part to an increase in the surface tension (σ) or viscosity (ŋ) of the liquid as the temperature decreases, or it may be due to a rise in the vapor pressure of the medium (P_V) (Mason and Lorimer 1988). Overall then, the general conclusion is that cavitation bubbles are more easily produced as the temperature is raised. Unfortunately the effects resulting from cavitational collapse are also reduced. A further factor which must be considered is that at higher temperatures approaching solvent boiling point large numbers of cavitation bubbles are generated concurrently. These will act as a barrier to sound transmission and dampen the effective ultrasonic energy from the source which enters the liquid medium. For this reason, if a liquid is sonicated at its boiling point, sonication would not be expected to generate any great ultrasonic effects. In other words, to get maximum cavitational benefit, any ultrasound experiments should be conducted at as low a temperature as feasible or with a solvent of high surface tension and high viscosity or low vapor pressure at the chosen temperature.

3.4.5 Dissolved gas and particles

Estimates of the acoustic pressure necessary to cause cavitation in water have led to a value of approximately 1,500 atm (Mason and Lorimer 1988). In practice, cavitation occurs at considerably lower values (< 20 atm) and this is undoubtedly due to the presence of weak-spots in the liquid which lower the liquid's tensile strength. There is, for example, sufficient experimental evidence to suggest that one cause of weak-spots is the presence of gas molecules in the liquid. It has been observed that the degassing of liquids leads to an increase in the cavitation threshold, *i.e.* to an increase in the values of applied acoustic pressure necessary before cavitation bubbles are observed (Mason and Lorimer 1988). It has also been found that the presence of particles, and more especially the occurrence of trapped vapor-gas nuclei in the cavities and recesses of these particles, lowers the cavitation threshold. For this reason, increasing the gas content of a liquid leads not only to a lowering of the cavitational threshold but also to a lowering of the intensity of the shock wave released on the collapse of the bubble. The threshold is lowered as a consequence of the increased number of gas nuclei (or weak-spots) present in the liquid, whilst the cavitation collapse intensity is decreased as a result of the greater cushioning effect in the bubble. If a soluble gas is used this will also provide large nucleus in the solvent. The greater the solubility of the gas, the greater the intensity of the shock wave created on bubble collapse. A further factor reducing the intensity of collapse may be that the more soluble the gas, the more likely it is to redissolved in the medium during the compression phase of the acoustic cycle.

3.4.6 Pressure

Increasing the external pressure (P_h) leads to an increase in both the cavitation threshold and the intensity of bubble collapse (Mason and Lorimer 1988). Greater ultrasonic energy is required to induce cavitation. Qualitatively, it can be assumed that there will no longer be a resultant negative pressure phase from the sound wave and so cavitation bubbles cannot be created. Clearly, a sufficiently large increase in the intensity of the applied ultrasonic field (I) could produce cavitation even at high overpressures. Increasing the value of P_h will lead to a more rapid and violent collapse.

3.4.7 Attenuation of ultrasound

For a variety of reasons the intensity of ultrasound is attenuated, i.e. it decreases as it progresses through a medium. Such reasons are for example the spreading of the ultrasound beam, scattering, and absorption due to various mechanisms (Ensminger 1988). If the acoustic impedance between the transducer and medium is small only some of this energy is dissipated in the form of heat, and there is little appreciable heating of the bulk medium during sonication (Mason 1991a). The extent of attenuation is inversely related to the frequency. In order to achieve identical intensities at a given distance in a medium it will be necessary to use a higher initial power for the source with the higher ultrasound frequency.

3.5 Power ultrasound applications

There are a number of low-intensity applications of ultrasonic energy, including process control, non-destructive testing, intrusion detecting, measurements of elastic properties, medical diagnosis, delay lines, signal processing, and appliance controls (such as television-channel selectors) (Ensminger 1988). Because this work concentrates on high-intensity or power ultrasound applications, those are considered more closely.

High-intensity applications of ultrasonic are those which produce changes in or effects on the media, or the contents of the media, through which the waves propagate. Various mechanisms may be activated by ultrasonic energy to promote such effects, but the mechanisms involved are not always known or understood. Most of the effects can probably be attributed to the following (Ensminger 1988):

1. Heat: as ultrasound progresses through a medium, energy is lost to the medium in the form of heat. Losses vary according to the nature of the medium. At certain interfaces, absorption may be high because of factors such as shear (friction) across the interface.
2. Stirring: intense ultrasound will produce violent agitation in a liquid medium of low viscosity and disperse material through the resulting currents of liquid or acceleration imparted to the particles.

3. Cavitation: many of the effects associated with ultrasound occur in the presence of cavitation. Emulsification of otherwise immiscible liquids occurs under this condition.
4. Chemical effects: chemical activity, especially oxidation reactions, may be accelerated, sometimes manifold, under the influence of ultrasonically produced cavitation. The effects have been variously attributed to heat and to homolytic rapture (radical formation) of chemical bonds. In some cases, the effect is a result of mechanical mixing or of dispersion of saturated layers that ordinarily form at an interface between the participants in the reaction.
5. Mechanical effects: stresses developed in the ultrasonic field can cause ruptures to occur in materials. They may also cause relative motion between surfaces, which produces selective absorption at these surfaces, as in the ultrasonic bonding of materials. Stresses developed in cavitation bubble walls can cause severe erosion of surfaces.
6. Electrolytic effects: there are indications that when two metals separated on the electrolytic scale even to a slight degree are exposed to intense ultrasonic irradiation in water, an accelerated galvanic action may be induced which causes electrolytic corrosion.
7. Diffusion: ultrasonic energy promotes diffusion through cell walls, into gels, and through porous membranes.
8. Vacuum effects: during the low-pressure phase of each cycle, boiling in liquids may be induced and fluids may be drawn into tiny pores.
9. Cleansing: sometimes the observed effects may result from acoustic eroding of a protective coating from a surface so that reactions between two materials may occur that would not be possible otherwise.

Although the mechanism may not be understood and unexpected effects are often produced, all the effects encountered have logical explanations (Ensminger 1988).

4. Ultrasound-assisted degradation of polymers

4.1 Introduction

Various methods such as the application of heat, light, microwaves, x- or γ-rays, chemical reagents, and ultrasonic radiation can cause polymer degradation. The application of ultrasonic energy for polymer degradation dates back to the 1930s when natural polymers were subjected to sonication, which resulted in a reduction in viscosity (Price *et al.* 1994). Suslick (1988) reported that the first experiments in 1939 showed that ultrasonic irradiation depolymerized starch, gum arabic, gelatine, and polystyrene. These studies were followed by detailed examinations of sonochemical polymer degradation by many researchers.

4.2 Factors affecting degradation

Mason and Lorimer (1988) suggested that the frictional and impact forces needed for polymer breakdown are the consequence of cavity collapse and they calculated that there is a lower limit of relative molecular mass (RMM) below which degradation ought not to occur. Price et al. (1994) claimed that this limiting molecular mass has the added effect of narrowing the molecular mass distribution. Mason (1991a) and Kuijpers et al. (2004) also showed that ultrasonic degradation, unlike chemical or thermal decomposition, is a non-random process, in which cleavage takes place roughly at the center of the molecule. Mason (1991a) also reported that degradation is fastest with larger molecules. It has been noticed in earlier studies reported by Mason and Lorimer (1988), that the rate of ultrasonic depolymerization decreases with decreasing molecular mass of the polymer, and that the initial structure of the molecule, rather than its size, determines whether it will be broken by this means. For example, Mason and Lorimer (1988), Mason (1991b), Lorimer et al. (1995), and Lorimer and Mason (1995) reported that the rate and the extent of degradation depends on the duration of irradiation, the concentration of the solution, the nature of the polymer and solvent, and the intensity of the ultrasound.

4.2.1 Frequency of ultrasound

The general conclusion that higher irradiation frequency is linked to a lower degradation rate is a view now shared by most workers in the field. Price *et al.* (1994) found that there were changes in the molecular mass distribution of a dextran sample at a frequency of 1.1 MHz, but no changes were found at a frequency of 3.3 MHz. Portenlänger and Heusinger (1997) noticed that the molecular mass distribution of dextran was dependent on frequency. The lower the frequency the more significant the changes were in the molecular mass distribution. It is also known that the higher the frequency of the ultrasound wave the more rapidly it is attenuated in the medium. Thus it is important to recognize that when comparing the effects of frequency, ultrasound intensity must be held constant. However, what is known is that the higher the applied frequency the shorter the period is in which bubble growth and collapse can occur and the more likely it is that there is insufficient time to produce cavitation. According to Mason and Lorimer (1988), there is a frequency limit (~10 MHz) above which cavitation does not occur. Some researchers have suggested that there is an optimum frequency at which the cavitation intensity attains maximum value and at this frequency maximum degradation occurs. For example, Mason and Lorimer (1988) reported maximum degradation at 1 MHz for polystyrene in benzene. In their view, the small observed degradation at the highest frequency (2 MHz), where presumably cavitation is negligible, is probably due to some kind of resonance effects.

4.2.2 Intensity of ultrasound

If degradation of polymers is due to cavitation then it is expected that degradation will only occur when the cavitation threshold is exceeded. This is confirmed by Mason and Lorimer (1988), who observed that the start of degradation coincides with the onset of cavitation. They found that the relative viscosity of the polystyrene in toluene after 90 minutes' ultrasound irradiation showed very little reduction beyond an input power of 10 W/cm^2.

Some researchers have observed that the degradation rate and extent of degradation increase with an increase in intensity. For example, Lorimer and Mason (1995) and Lorimer *et al.* (1995) studied the effect of ultrasound power on the degradation of dextrans and found that the higher the sonication power at a particular temperature and concentration, the faster the degradation rate is. Li *et al.* (2005a) found that the degradation of polystyrene is faster and proceeds futher at higher ultrasound intensity. Ebringerová and Hromádková (1997) and Ebringerová *et al.* (1997) observed that the degradation of corn hull xylan and corn cob xylan is dependent on the ultrasonic power. At higher sonic power and with a longer irradiation time, a high molecular fraction was slightly moved to a lower elution volume and a low-molecular fraction appeared. Yuntao *et al.* (2005) noticed that with an increase in ultrasonic intensity the weight average and number average molecular mass of high-density polyethylene melt decreases and the molecular weight distribution moves in the direction of low molecular mass, indicating that the extent of degradation of high-density polyethylene melt increases with a rise in ultrasonic intensity. Mason and Lorimer (1988) reported when using polystyrene in benzene or poly(methyl methacrylate) in chloroform, and Keqiang *et al.* (1985 and 1986) when using hydroxyethylcellulose and polyethylene oxide in aqueous solution, that degradation increases with an increase in intensity.

In addition, some other researchers have suggested that there is an optimum power which can be applied to a system to obtain the most beneficial effect. For example, Czechowska-Biskup *et al.* (2005) studied the influence of ultrasound power, *i.e.* ultrasound intensity, on the efficiency of chitosan degradation. In their study the sonication time was inversely proportional to the ultrasonic power, so that a constant amount of ultrasonic energy was always absorbed. They found that degradation is not efficient at low power. They explained that this can be attributed to the fact that in order to induce cavitation, the ultrasound power must reach some minimum value and the lowest power they used was close to that threshold. However, in the dose range 40–80 W the degradation yield was stable, while it seemed to decrease again at the highest power of 100 W. Czechowska-Biskup *et al.* (2005) have reported that it is known that at high power the efficiency of sonochemical prosesses may be diminished, since the cavitation bubbles present at high concentration may scatter the ultrasound waves. Qualitatively, it could be said that the number of bubbles produced at very high intensities serves to reduce power dissipation by reflecting the sound wave and creating a non-linear response to the increase in intensity. It can also be argued that at high intensities the cavitation bubbles have grown so large on rarefaction that there is insufficient time available for collapse during the compression cycle.

4.2.3 Solvent

Most of the experimental data indicate that there is a decrease in the extent of depolymerization with increasing solvent vapor pressure. For example, Madras and Chattopadhyay (2001a) observed that the degradation of poly(vinyl acetate) is less efficient in solvents at higher vapor pressure. Chakraborty *et al.* (2004) also found that the degradation rate of polybutadiene and isotactic polypropylene decreases with increasing solvent vapor pressure. Mason and Lorimer (1988) found that this is also the case when the viscosities of solvents are similar. Basedow and Ebert (1975) have investigated the effect of ultrasound on the degradation of dextran in several solvents and found that the solvent characteristics have a considerable effect on the degradation rates and that there is a relationship between the degradation rate constants and the enthalpy of vaporisation of the solvent. However, quite often the viscosities are also different. Although the amount of degradation increases with a decrease in solvate vapor pressure, the order is also that of increasing solvent viscosity. Chakraborty *et al.* (2004) reported that better transmission of shock waves in a solution of higher kinematic viscosity is a probable reason explaining the increase in the degradation rate coefficients of polybutadiene and isotactic polypropylene at increasing kinematic viscosity. For this reason, while vapor pressure may be the major solvent factor involved in the degradation process there could also be a contribution from solvent viscosity or even, though less likely, from surface tension. Desai *et al.* (2008) reported that solvents with higher surface tension offer higher resistance to the formation of cavities in the system and hence the expected cavitational intensity is higher, resulting in a higher extent of degradation. Although an increase in viscosity makes it more difficult for cavitation to occur (Chapter 3.4.3), the pressure effects resulting from bubble collapse will be greater (providing that cavitation occurs at all). In other words, the cavitational effects of increasing vapor pressure and viscosity are partially compensatory, *i.e.* act in opposite directions.

4.2.4 Temperature

One way to raise the vapor pressure of a solvent is to increase the temperature. The consequence of this should be a decrease in the rate of degradation as a result of the lower intensities of cavitation collapse at the high temperatures. This prediction has also been verified in practice. For example, Lorimer and Mason (1995) and Lorimer *et al.* (1995) studied the effect of temperature on the rate of degradation of native dextran. They found that the lower the temperature at a particular sonication power and concentration, the faster the degradation rate. Vijayalakshmi and Madras (2004) observed that the degradation rate coefficient decreases with increasing temperature and attributed this to the higher vapor pressure and lower viscosity at higher temperature. Chakraborty *et al.* (2004) with polybutadiene and isotactic polypropylene and Trciński and Staszewska (2004) with chitosan observed a decrease in degradation with an increase in temperature. Chakraborty *et al.* (2004) reported that as the temperature of the solution increases, a large quantity of the solvent vapor enters the cavitation bubbles during their expansion and exerts a cushioning effect during collapse, leading to diminished intensity of the shock wave, reducing the jet velocity and leading to reduced degradation at higher temperatures. However, Petit *et al.* (2007) observed no change in the depolymerization process with exopolysaccharide in the studied temperature range. They reported that this could be the consequence of a compensation effect, due to the increase in viscosity with temperature.

4.2.5 Molecular mass and concentration of polymers

The degradation of the same polymer samples of various RMM has been studied. For example, Basedow and Ebert (1975), Mason and Lorimer (1988), Lorimer *et al.* (1995), Madras *et al.* (2000), Xiuyuan *et al.* (2001), Kuijpers *et al.* (2004), Li J. *et al.* (2004 and 2005), Li Y. *et al.* (2005), Waskiewicz *et al.* (2005), Vodeničarová *et al.* (2006), Petit *et al.* (2007), Desai *et al.* (2008), and Kobayashi *et al.* (2008) found that the degradation rate of polymers was highest for the sample with the largest RMM and/or that the degradation had a certain limiting value after which no degradation occurred. The effect of polymer solution concentration on degradation has also been studied and, for example, Mason and Lorimer (1988), Kanwal *et al.* (2000), Xiuyuan *et al.* (2001), Trciński and Staszewska (2004), Waskiewicz *et al.* (2005), Petit *et al.* (2007), and Desai *et al.* (2008) have reported that in every case the rate and the extent of degradation decrease with an increase in polymer concentration. However, cavitation is difficult to achieve in viscous materials corresponding to high RMM polymers. For example, Desai *et al.* (2008) reported that it should be noted that the intensity of cavitation drops remarkably with an increase in the viscosity of the medium. For this reason, dilute solutions of polymers have been used for the study of ultrasonic depolymerization. It is known that the formation of cavitation in the liquid requires that the negative pressure in the rarefaction region of wave function must overcome the natural cohesion forces acting within the liquid. Therefore, cavitation should be more difficult to produce in viscous liquids, where the forces are stronger and waves with greater amplitude and hence greater intensity will be necessary. Thus, the higher the viscosity the more difficult it becomes to cavitate the solution at a given intensity and the smaller the degradation effect is. On the other hand, the effects of cavitation collapse in viscous liquids are stronger than collapse in less viscous liquids.

Lorimer and Mason (1995) studied the effect of ultrasound on the degradation of native dextran and found that the lower the concentration at a particular temperature and sonication power, the faster the degradation rate is. They also found that the “apparent” limiting RMM of native dextran is between 50,000 and 80,000 g/mol. Price (1996) studied the effect of ultrasound on the degradation of polystyrene and found that degradation proceeds more rapidly for higher molecular masses and approaches a limiting value (M_{lim}) below which no further degradation takes place, in his case ca. 30,000 g/mol. Portenlänger and Heusinger (1997) observed that when using dextrans in aqueous solutions there was a stronger increase in polymer degradation with increasing molecular weight. Taghizadeh and Mehrdad (2003) studied the effect of concentration of polyvinyl alcohol on polymer degradation. Their results indicate that the extent of degradation is more pronounced in more dilute solutions. Harkal *et al.* (2006) also found that at higher concentration the intensity of the cavitation phenomenon is depressed and therefore the extent of polymer chainbreaking decreases. Czechowska-Biskup *et al.* (2005) found that the degradation of chitosan decreases with increasing polymer concentration. They reported that the decrease is most probably due to an increase in viscosity of the solution, which is a parameter that reduces the intensity of cavitation. However, Vijayalakshmi and Madras (2005) reported that the degradation rate coefficient is independent of the initial molecular mass. Based on their experimental data on the ultrasonic degradation of poly(ethylene oxide) in various solvents, it was concluded that the effect of the vapor pressure of the solvent plays a cruicial role in determing the degradation rate compared to the effect of the polymer-solvent interactions studied.

4.3 Degradation mechanisms

It is well established that prolonged exposure of solutions of macromolecules to high-energy ultrasonic waves produces a permanent reduction in viscosity (Mason and Lorimer 1988). Even when the irradiated polymers are isolated and redissolved, their viscosity remains low compared to non-irradiated solutions. The exact mechanism by which degradation occurs is still open to discussion, with various models being proposed (Suslick 1988). It is generally agreed that hydrodynamic forces are of primary importance. Hydrodynamic forces may originate as a result of increased frictional forces between the ultrasonically accelerated faster-moving solvent molecules and the larger, less mobile, macromolecules. Doulah (1978) suggested that hydrodynamic forces may also be due to the high-pressure shock waves associated with the collapse of cavitation bubbles. The results of his experiments indicated that the degradation rate is dependent upon acoustic intensity, the size of the macromolecule, and suggested that there is a minimum chain length below which degradation does not occur. On the other hand, for example, Ramsden and McKay (1986) have shown that it is also possible that the main chain scissions are secondary effects due to chemical reactions initiated by unstable intermediates, such as free radicals or ions, produced by ultrasound. Price *et al.* (1997) studied the production of hydroxyl radicals during ultrasound treatment. They found that clearly there is radical production at both frequencies studied (1.1 and 3.3 MHz) and that, as expected, radical production increased at higher intensities. Madras and Chattopadhyay (2001b) studied the ultrasonic degradation of poly(vinyl acetate) in the presence of benzoyl peroxide as an oxidizing agent. They found that, unlike thermal degradation, the presence of benzoyl peroxide lowered the degradation rate. Madras and Chattopadhyay (2001b) reported that a radical reaction mechanism explains their experimental results. Whatever the mechanism involved, depolymerization results in the homolytic breakage of covalent bonds in the macromolecule to produce long-chain radical entries. This has been established by Tabata and Sohma (1980a,b) when investigating the depolymerization process in the presence of various radical scavengers. Waskiewicz *et al.* (2005) reported that ultrasonic degradation undergoes a different mechanism than ultraviolet and gamma degradation – probably a mechanical one.

If polymer degradation observations are the result of cavitation, then the extent of degradation should be zero if the process is carried out under conditions which eliminate cavitation, *i.e.* either *in vacuo* or at high overpressure (Mason and Lorimer 1988). These conditions can be achieved by degassing the solution or by increasing the external pressure. Both degradation *in vacuo* and at high overpressure have been observed. To explain these observations, it has been suggested that the decrease in solution viscosity on irradiation are the consequence of degradation of the polymer, as a result of increased frictional forces between the ultrasonically accelerated faster-moving solvent molecules and the larger less mobile macromolecules. Although different modes of interaction between the solvent and polymer molecules have been envisaged, it has been concluded that the increased forces are sufficient to break a C-C bond.

5. Ultrasound-assisted disintegration of sewage sludge as pre-treatment for anaerobic digestion

5.1 Introduction

Large quantities of biomass – sludge – are produced in biological wastewater treatment. Sewage sludge consists of water and solid matter. The biosolids predominantly consist of particulate microbial or plant cell material (Eder and Günthert 2002). Nickel (2002) reported that in Germany, for example, municipal wastewater treatment results in 60 million m^3 of sewage sludge each year. In agriculture about 190 million m^3 of liquid manure are produced in Germany. Further amounts of biosolids come from forestry and industrial food production. Treatment of such material requires several processes that include digestion, settling, and dewatering. The overall treatment procedure is referred to as stabilization since the sludge material continues to degrade with the evolution of noxious gases under ambient conditions and must be stopped, or stabilized, before it can be used or disposed of (Mason 2007b). Gogate and Kabadi (2009) also reported that because the sludge is highly susceptible to decay it has to be stabilized in order to enable environmentally safe utilization and disposal. Neis *et al.* (2001) and Mason (2007b) have reported that the standard stabilization technique for sludge is anaerobic digestion which results in reduced content of organic matter.

Nickel (2002) mentioned that in Germany, for example, more than 80% of sewage sludge is treated anaerobically, where the volatile compounds could be utilized as a source for renewable energy. This process yields a net reduction in biosolid mass and volume. A portion of the volatile solids (VS) is converted microbiologically into methane and carbon dioxide. This biogas is used for energy production. The final products are stable innocuous biosolids that can be used as fertilizer. For example, Nickel (2002) and Benadballah El-Hadj *et al.* (2007) have reported that the principal disadvantage of anaerobic biosolid fermentation is the rate-limiting long hydraulic retention time required for the conversion of particulate organics into biogas. Retention times in excess of 20 days result in high fermenter volumes and thus capital costs. Large converted tanks along with pumps for feeding and circulation, heat exchangers and gas mixing are required. Despite the long retention times during anaerobic digestion, no complete degradation of the biosolids is achieved, since because of the complex structures, the biosolids are only partially biodegradable. For example, the structure of biosolids appears to be important in controlling the rate and degree of degradation. In the case of sewage sludge fermentation, the reduction in VS ranges between 20% and 60%.

Eder and Günthert (2002) reported that the cells of the solid matters (microorganisms) are disrupted by disintegration and that cell liquid is released into the sludge water. Improved biodegradability of the organic substance in the sludge increases the biogas yield and decreases the mixed liquor volatile suspended solids in the digested sludge. Further ranges of the disintegration can be seen in the denitrification and in the dewatering of the digested sludge. The material-flow-management of sludge with disintegration leads to an increase in both productivity and efficiency.

As stated, the rate-limiting step in the anaerobic digestion process is slow biological hydrolysis and since one of the major effects of power ultrasound on micro-organisms is the breakdown of cell walls and the subsequent release of cellular material, sonication can be used to make the dissolved organic compounds more readily available in the anaerobic digestion process. As a result the fermentation rate is greatly improved as is biogas production.

5.2 Ultrasound – one method for sludge disintegration

The biodegradability of biosolids can be improved by solubilization. Positive effects have been shown for thermal pre-treatment, ozonation, chemical hydrolysis by acidification or alkaline addition, and mechanical disintegration (Nickel 2002 and Appels *et al.* 2008). Quarmby *et al.* (1999) found that sonication of sewage sludge can be used as pre-treatment for anaerobic digestion. The efficiency potential of this process lies in the break-up and solubilization of solid sludge particles. Onyeche *et al.* (2002) reported that one of the mechanical disintegration mechanisms is ultrasound pre-treatment, after which anaerobic digestion is accelerated, biogas production is improved and a reduction in the amount of sludge is observed. The major effects of power ultrasound on microorganisms are the breakdown of cell walls and the subsequent release of cellular material. This makes the dissolved organic compounds more readily available in the anaerobic digestion process and the fermentation rate is greatly improved. Sonication is also capable of improving settling through the removal of filamentous material, which is one of the reasons for flotation (Neis *et al.* 2001).

Bougrier *et al.* (2006) studied the effects of ultrasound, ozonation, and thermal pre-treatment. They found that all treatments lead to chemical oxygen demand and matter solubilization and have little influence on the mineral matter. In terms of solubilisation, thermal pre-treatment (170 or 190 °C) was found to be better than sonication or ozonation. But, in terms of anaerobic biodegradability, the best results were obtained with ultrasound and thermal treatment, which biodegraded sludge almost totally within 24 days of tests. Appels *et al.* (2008) reported that sonication is no doubt the most powerful method to disrupt sludge cells. Although cell disintegrations of 100% can be obtained at high power levels, power consumption then becomes a serious drawback. Bougrier *et al.* (2006) reported that it was impossible to determine whether sonication or thermal treatment is the best treatment method, because there was not enough difference between their sludge biodegradability results. So, in order to choose one treatment over the other, it is necessary to consider other parameters like costs, sanitation, simplicity of installation and so on. But in general, techniques other than ultrasonic disintegration have not as yet been successful technically and economically. There are dozens of wastewater treatment plants which have chosen ultrasound over anaerobic digestion for the pre-treatment process.

5.2.1 The effects of ultrasound frequency, intensity, sonication time, and ultrasonic specific energy

Tiehm *et al.* (2001) studied the effect of ultrasound frequency on sludge pre-treatment before anaerobic digestion. The ultrasound frequency varied within a range of 41 kHz to 3217 kHz. The impact of different ultrasound intensities and treatment times was also examined. Sludge disintegration was greatest at low frequencies. Short sonication times resulted in sludge flock deagglomeration without the destruction of bacteria cells. Longer sonication brought about the break-up of cell walls, sludge solids were disintegrated and dissolved organic compounds were released. The anaerobic digestion of waste activated sludge following ultrasonic pre-treatment causing microbial cell lyses was significantly improved. There was an increase in VS degradation as well as an increase in biogas production. The increase in digestion efficiency was proportional to the degree of sludge disintegration. To a lesser degree the deagglomeration of sludge flocks also augmented the anaerobic VS degradation. Wang *et al.* (1999) examined the effect of sonication time on sludge disintegration using batch system digesting and waste activated sludge (WAS). The pre-treatment times were 10, 20, 30, and 40 min. They obtained increases in methane compared to the respective control values of 12%, 31%, 64%, and 69%. A 200 W ultrasonic disintegrator (Kubota Insonator model 200M) was used at an oscillation frequency of 9 kHz.

Quarmby *et al.* (1999) compared the performance of anaerobic digestion on unsonicated sludge and sludge sonicated at two different intensities. The tests were run as a series of bath flasks and three 100 L anaerobic digesters. The data from the batch tests clearly indicated the positive effect on anaerobic digestion through gas production (increase of 15%) and volatile fatty acid production. The data from the anaerobic digesters were less distinct. Little difference was observed between the volumes of gas produced, although there was an increase in methane production, VS reduction, and soluble chemical oxygen demand (SCOD) by up to 6%, 5.5%, and 15%, respectively, when comparing the sonicated and unsonicated sludge. However, sonication was observed to have a detrimental effect on sludge dewaterability. This effect was more acute when a higher sonication intensity was used, although anaerobic digestion did reduce this effect. Therefore, while sonication can enhance anaerobic digestion, the negative effect on sludge properties must be considered before applying this technique to any site where dewatering processes are used. The two different sonication intensities indicated that there was a minimal difference in performance. For this reason, the application of low-intensity sonication offers both process and economic benefits.

Xie *et al.* (2009) found that low-intensity ultrasound at 35 kHz with an intensity of 0.2 W/cm^2 can promote the biological activity of anaerobic sludge remarkably. They also found that the activity of anaerobic sludge is significantly influenced by irradiation time. At an irradiation period of 10 min, the biological activity of sludge increased to the maximum, but as the irradiation time was prolonged, it decreased gradually. Xie *et al.* (2009) observed the marked influence of ultrasonic intensity and irradiation time and found the optimal ultrasonic condition. They concluded that the function of low-intensity ultrasound causes the cell to be hurt in some ways and makes the cell membrane flaw, promoting the permeability and selectivity of the cell membrane and wall and accelerating all sorts of nutrition or molecule transport between cell membranes. In addition, ultrasound can increase the activity of enzymes and modifies the metabolism of cells.

Casellas *et al.* (2009) studied the effect of different specific ultrasound energies on the disintegration of sludge. They found that total solids (TS), VS, total nitrogen, and chemical oxygen demand (COD) solubilization increase with increasing specific energy supply. In their study conditions (f = 20 kHz, power supply 60 W, TS = 17.8 g/L), flow cytometry experiments showed that organic matter solubilization was not due to cell membrane breakage but more probably to flock breakage. Shen *et al.* (2007) also studied the influence of ultrasonic specific energy on sludge decomposition. They found that ultrasound irradiation can increase the SCOD of the sludge supernatant remarkably, which increased with ultrasound intensity and irradiation time. Benadballah El-Hadj *et al.* (2007) studied the effect of specific ultrasound energy on sludge disintegration and on anaerobic digestion efficiency using methane production measurements in their biodegradability test. They found that under both mesophilic and thermophilic conditions biogas production was improved with increasing specific ultrasound energy input. They also found that mesophilic anaerobic fermentation is more readily ultrasonically influenced than thermophilic anaerobic fermentation. Since the hydrolysis of organic matter is higher at thermophilic conditions, solubilization by ultrasound would affect mesophilic digester performance more. Bougrier *et al.* (2005) also studied the effect of specific ultrasound energy on sludge disintegration. They observed that ultrasound leads to an increase in sludge biodegradability, but that sludge was not fully biodegradable. At low specific energiy supply biogas production was the same, which can be explained by variation in particle size. Energy was used to reduce flock size, not to break cells. After that biogas production increased with greater ultrasonic energy supply and for each ultrasound treatment, biogas production was higher than that for untreated sludge. Dewil *et al.* (2006) reported that the release of COD from the sludge phase into the filtrate phase is a function of the specific ultrasound energy input. A major fraction of the COD is transformed into biodegradable organics.

5.2.2 The effects of sludge temperature, sludge pH, sludge concentration, and each sludge part

Shen *et al.* (2007) studied the influence of temperature on sludge decomposition. Their studies at 28.7 kHz ultrasound frequency showed that sludge temperature increases more quickly when the ultrasound intensity is higher or the treating time is longer. They also noticed that without ultrasound the decomposition caused by heat was very small. At the same temperature, the SCOD after ultrasound was two times as high as that without ultrasound. Shen *et al.* (2007) also found that when temperature was controlled, SCOD increased more slowly than without temperature control. Thus heating caused by ultrasound irradiation is not the main factor in sludge decomposition, but it does contribute to the decomposition.

Wang *et al.* (2005) found that ultrasonic density, *i.e.* ultrasonic power level (W/ml), ultrasonic intensity, disintegrated sludge pH, and sludge concentration have an impact on sludge disintegration (20 kHz). Based on kinetic models, ultrasonic disintegration was impacted in the order: sludge pH > sludge concentration > ultrasonic intensity > ultrasonic density. They determined that hydro-mechanical shear forces are predominantly responsible for ultrasonically activated sludge disintegration, and that the contribution of the oxidizing effect of hydroxyl radicals HO• becomes greater as ultrasonic intensity is increased.

An improvement in the biological activity of ultrasound pre-treated sludge was also successfully demonstrated using laboratory-scale reactors by Schläfer *et al.* (2000 and 2002). All the experiments showed improved gas production compared to untreated sludge samples. The results indicate that increased sludge concentration and disruption time lead to increased specific gas production. After laboratory-scale studies they developed a pilot-scale (200 L) bioreactor. Batch experiments were made by measuring the degradation rate of organic compounds of wastewater. The process parameters were kept constant while varying the ultrasonic (US) intensity. The most important aspect of the experimental results was that a more than 100% increase in the maximum biological degradation rate was achieved by ultrasound transduction with an optimum US intensity of 1.5 W/L at 25 kHz. Very low ultrasonic power led to a decrease in the degradation rate down to the reference value. Implementation of an overly high level of ultrasound led to a drastic decrease in biological activity to a level far below the reference value. The researchers claimed that their bioprocess reduced overall energy by using low-energy ultrasonic irradiation below the cavitation level. The ultrasound-assisted biological degradation process should be presented together with its optimization and the economical calculation.

Show *et al.* (2007) examined the role of sonication time, sonication density, *i.e.* ultrasonic power level (W/ml), type of sludge, and solid content in ultrasound sonication. They found that the best ultrasound disruption effects were associated with secondary sludge at higher sonication density within an optimum total solids content ranging between 2.3% and 3.2%. Gonze *et al.* (2003) also studied the effect of sludge concentration on disintegration. They found that for a given dissipation of energy, the quantity of disintegrated particles will be much greater with concentrated sludge than with diluted sludge. This is due to the fact that particle disruprion is limited by the probability of an imploding cavity meeting a particle. This fact is important because it means that from the industrial development standpoint, it is better to apply the process to concentrated sludge. However, van Leeuwen *et al.* (2006) reported that sludge disintegration efficiency declines significantly at higher TS content. Thus there is a limiting TS concentration that could be effectively disintegrated by ultrasound, and this is governed by the capability of an ultrasonic unit to produce cavitation.

Bougrier *et al.* (2005) also studied the effect of each sludge part (soluble and particles) on biogas production. They found that the volume of biogas produced with the soluble part of sludge increased with specific supplied energy, whereas the volume of biogas produced with the particulate fraction was quite constant. They observed that for non-treated sludge, biogas was produced from the particulate matter at a rate of 97%, whereas for ultrasonically treated sludge biogas was produced from the particulate matter at a rate of 60% only. Total biogas volume increased because more matter was soluble. The solids contained in the particulate part of the sludge were made soluble due to the ultrasound. They were more available for bacteria in the soluble fraction, and thus biogas production increased. Chu *et al.* (2001) reported that for the original sludge most COD is associated with the solid phase rather than the soluble form. At a low ultrasound power level (0.11 W/mL, 120 min), the SCOD did not significantly change, but at 0.33 W/mL about 20% of the total COD was transformed into soluble form after 120 min sonication. The COD in soluble form thereby increased by 40 times after ultrasonic treatment. At the same time the ratio of biochemical oxygen demand (BOD) and total chemical oxygen demand (TCOD) increased from 66% to around 80%, indicating that most of the released COD is biodegradable. Feng *et al.* (2009) also observed that ultrasonication increased the transfer of COD from the particulate fraction to the soluble fraction, and there was a strong, positive correlation between SCOD and the applied ultrasound energy dosage. He *et al.* (2008) observed that the SCOD/COD ratios after ultrasound pre-treatment were greatly changed, suggesting that a large amount of insoluble organics of sludge flocks were transferred into soluble organics. The increase in SCOD may result from the destruction of flock structure after ultrasonic pre-treatment, promoting the release of colloidal and soluble organics into the solution. The steady increase in SCOD during sonication might have originated from the release of extracellular polymeric substances (EPS), such as polysaccharides, proteins, nucleic acids, lipids, and other polymeric compounds, during flock disintegration and the release of cell components during cell lysis (Zhang *et al.* 2007).

Zhang *et al.* (2009) studied the effect of sludge organic content (VS/TS), solid concentration, ultrasonic intensity and ultrasonic treatment time on disintegration. They found that higher VS/TS benefited sludge sonication. Below the optimal TS range, TS increase provided more organic substances to be transferred into water and thus improved sludge lysis. Above the optimal TS range, too many solids hindered sound transfer and lowered the ultrasound energy efficiency. The sound intensity threshold for sludge was found to be 20–30 W/cm^2 with most profound sludge lysis in the initial period of sonication. In terms of energy efficiency and sludge lysis efficiency, the following optimal operational conditions were proposed: sludge TS of 20–30 g/L, sound intensity of 158–251 W/cm^2, and sonication time of 5–15 min.

5.2.3 Residence time of the digesters

Tiehm *et al.* (1997) studied the effect of ultrasound on sludge pre-treatment using ultrasound at a frequency of 31 kHz and high acoustic intensities. Ultrasound treatment resulted in raw sludge disintegration through an increase in COD in the sludge supernatant and size reduction of sludge solids. Semi-continuous fermentation experiments with disintegrated and untreated sludge were performed for four months on a semi-technical scale. One fermenter was operated as a control with a conventional residence time of 22 days. Four fermenters were operated with disintegrated sludge and residence times of 22, 16, 12, and 8 days. In the fermenter operated with residence time of 22 days, the reduction in VS was 45.8% for untreated sludge and 50.3% for disintegrated sludge. The fermentation of disintegrated sludge was stable even at the shortest residence time of 8 days with biogas production 2.2 times that of the control fermenter. Clark and Nujjoo (2000) demonstrated the influence of the hydraulic retention time (HRT) on the gas yields from sonicated sludge. With a mesophilic digester they obtained a 61% increase in specific methane yield at a 15 day HRT. Bougrier et al. (2006) also reported that ultrasound pre-treatment accelerates sludge degradation. For untreated sludge, it took 24 days to produce 300 mL of biogas per gram of COD added, while in the case of sonicated sludge it took only 6 days to produce the same amont of biogas.

Nickel and Neis (2007) reported pilot- and full-scale ultrasonic disintegration studies of biosolids. They found that at a sludge residence time (SRT) of 8 days, ultrasonic disintegration of WAS enhanced the degree of anaerobic disintegration by more than 40%. The highest rate of VS degradation was obtained at the shortest SRT (4 days). The data demonstrated that the anaerobic degradation process is considerably accelerated by ultrasonic sludge pre-treatment. Yin *et al.* (2006) observed that ultrasound treatment (20 kHz; 600 W/m^2; 1 min) enhances anaerobic digestion and reduces digestion time. At the same resolution ratio, say 49%, the digestion time of sludge with ultrasound pre-treatment was 7 days less than that without ultrasound.

Forster and Lafitte-Trouqué (2004) studied the influence of ultrasound and γ-irradiation on the digestion of sludge. The sonic conditions were a processing time of 90 s, a frequency of 23 kHz, a power of 47 W and a γ-irradiation dose of 500 krad. The thermophilic and mesophilic digesters (35 °C or 55 °C) were operated in a semi-continuous mode, being fed with fresh WAS every 24 h at HRT of 8, 10, and 12 days. Prior to any treatment, the WAS was thickened to give total solids (TS) concentrations of 20–25 g/L. The differences between the digesters, in terms of VS reduction and biogas production, were not statistically significant for any particular set of conditions. Thermophilic digestion performed better than mesophilic digestion in terms of biogas production, VS reduction, and specific methane yield. The optimum retention time was 10 days at both temperatures. The results obtained in the study led to the conclusion that pre-treatment with ultrasound, at an applied dose of 3.4–5.0 kJ/g VS, or with γ-irradiation (with a dose of 500 krad) did not significantly improve the anaerobic digestion in terms of solids removal, biogas production and specific methane yields. However, a significant improvement was seen in the hourly biogas production study at the thermophilic temperature with an HRT of 10 days over the first eight hours.

5.3 Ultrasound-assisted disintegration on full scale

Xie *et al.* (2007) reported ultrasound disintegration technology tests conducted in the field under tropical conditions with a full-scale ultrasonic facility and two 5000 m^3 digesters (control and test). Each digester was fed with mixed primary (one-third) and thickened activated (two-thirds) sludge of identical quality and volumes of up to 200 m^3/d. For both digesters, all the operating conditions were the same except for the inclusion (test) and omission (control) of the ultrasonic device to pretreat the sludge feed. The ultrasound facility consisted of five sets of a 20 kHz ultrasound generator, converter, booster and sonotrode, and one V-shaped reactor chamber housing five donut-shaped horns stacked one to top of another with a clearance of 5 cm. The power rating of the sonotrode was 6 kW. Under normal operating conditions, the power level of the ultrasound device was controlled at $\leq$ 50% of the maximum value. In comparison with the control, the five-month field study showed that ultrasound pre-treatment of sludge increases daily biogas production by up to 45%. There were no significant differences in biogas composition from the two digesters. When translating the increase in biogas production to its source (volatile suspended solids), an increase is sludge solids removal of up to 30% can be expected under optimal operation conditions.

After pilot-scale tests, Nickel and Neis (2007) focused their study on full-scale experiments. Ultrasound equipment has already been installed on a full scale in a number of wastewater treatment plants in several countries. As compared to mechanical, thermal, and chemical disintegration methods, ultrasound application shows significant advantages especially with regard to operating conditions: ultrasonic reactors are very compact, simple to install and easy to operate. Nickel and Neis (2007) listed the requirements for a full-scale ultrasound reactor operating in a wastewater treatment plant:

- capacity for treating large volumetric sludge flows
- capacity to accept varying sludge properties (solids concentration, viscosity)
- removal of coarse and shaggy impurities prior to sonication to avoid reactor blocking
- automatic control of operation.

Appels *et al.* (2008) reported that ultrasound treatment units are commercially available in a wide range of capacities (between 1 and 20 kW) and modular layout. The capital costs today are roughtly € 20,000 /kW, with 1 kW capable of treating sludge from a wastewater treatment plant of 10,000 population equivalent (P.E.). Operating and maintance costs are minimal although the ultrasound probes need replacement avery 1.5–2 years. Using ultrasound treatment improved VS destruction by between 40% to 50%, enhancing biogas production by about 50%. The savings are approximately € 1.5–2/P.E./year. Since the degradation rate is accelerated, the dimension of the digesters can moreover be reduced for a given load, thus reducing the impact of high capital requirements. Khanal *et al.* (2007) summarized in their review article that published studies showed an improvement of as much as 40% in solubilization of WAS following ultrasonic pre-treatment. Both laboratory and full-scale studies showed that the integration of an ultrasonic system in the anaerobic digester improved anaerobic digestibility significantly.

6. Ultrasound-assisted remediation of contaminated soil

6.1 Introduction

Mason (2007a,b) reported that for contaminated soil wastes the currently available options for management and disposal are principally:

- Permanent storage in a secure ladfill. This will result in a permanent retained liability by the waste generator.
- Incineration in a permitted waste incinerator. This is costly and entails the risk of atmospheric emissions.
- Soil washing to produce bulk soil with low-level contamination. However, the washing process itself will produce a volume of solvent that must be treated before disposal.

For many years ultrasound has been considered as a technology to promote the process of soil washing and if subsequent disposal of the washings was considered at all this was perhaps to be a separate treatment. An integrated system has been developed in Canada (by Sonic Environmental Solutions Inc.) for large-scale continuous processing using acoustic frequencies in the audible range that incorporates the clean-up of the washings and recycling of the solvent. There is also one commercial remediation technique where ultrasound has been used as an aiding technique. The vibrating tray (Advanced Sonic Processing Systems, USA) using 20 kHz magnetostrictive transducers most resemble the technique under development.

Collings *et al.* (2006) reported that high-power ultrasonic technology offers several advantages comparated to current soil remediation methods. These include high destruction rates, the lack of dangerous breakdown products, and the low energy demands, assuming that similar rates of destruction to those obtained in laboratory or pilot-scale studies can be obtained at an industrial scale. A further advantage is that the technology can be made quite compact and transportable, allowing on-site treatment and the convenience of hydraulic transport of soil in slurries of typically 40% by weight.

Hintikka *et al.* (1999, 2001, and 2002) reported that separation techniques used in the mining industry, such as screening, heavy medium separation, and flotation, have recently been successfully applied to the remediation of soils contaminated by heavy metal like bullets, broken parts thereof, and alteration products. Soil remediation using mineral processing methods aided by power ultrasound is a novel method, where the effects of power ultrasound are used to further improve the operation of these mineral processing techniques. The ultrasound, which was used instead of attrition conditioning, was expected to produce less fine material than traditional methods.

Power ultrasound can be used for the rehabilitation of industrial sites or the reclamation of polluted land by the removal of chemical and biological contamination from the soil. For example, Newman *et al.* (1997), Singh and Singh (1997), Farmer *et al.* (2000), Feng *et al.* (2001), Meegoda and Perera (2001), and Swamy and Narayana (2001) have successfully used ultrasound to clean organic or inorganic matter from various particle surfaces. There are two basic mechanisms through which this can occur: either via the removal of contaminated material from the surface of soil particles or the leaching-out of more deeply entrenched materials.

6.1.1 Surface cleaning of particles

Mason (1999) reported that many conventional soil washing processes are based on the principal that pollutants absorb into the very small particulate components of the soil such as silt, clay, and humic matter, which tend to be attached to coarser sand and gravel particles. These larger particles make up the majority of the soil content. A primary aim in soil washing is therefore to dislodge and separate these fine components from the bulk soil. If the pollutant materials can be detached from the bulk, possibly together with some other surface contamination, a concentrated volume of polluted soil can be produced. This can then be treated or disposed of, and a large volume of residual soil which requires relatively little treatment can be returned to the site as re-fill.

6.1.2 Leaching of pollutants from soil

Any improvement in the penetration of solvent into particulate matter will result in the enhanced removal of soluble material, which may be trapped inside the solid particles. This process is referred to as ultrasonic leaching and has been investigated by Narayana *et al.* (1997) in hydrometallurgy for the removal of metals from ores. Dramatic increases in leaching rates induced by ultrasonic irradiation have been reported for many ores. This process is referred to as ultrasonic leaching and has been investigated for the decontamination of different types of soils, *e.g.* landfills, mining spills, and river sediments. Batch tests for accelerating leaching have used ultrasound for the removal of radio nucleotides and heavy metals from soils. The application of ultrasound has also been found to aid precious metal recovery from waste products, including industrial, municipal, and mine wastes. Although there is plenty of experimental evidence that ultrasound improves leaching the exact mechanism is not fully understood. Swamy and Narayana (2001) have suggested models for leaching in the absence and presence of ultrasound (Fig. 3.).

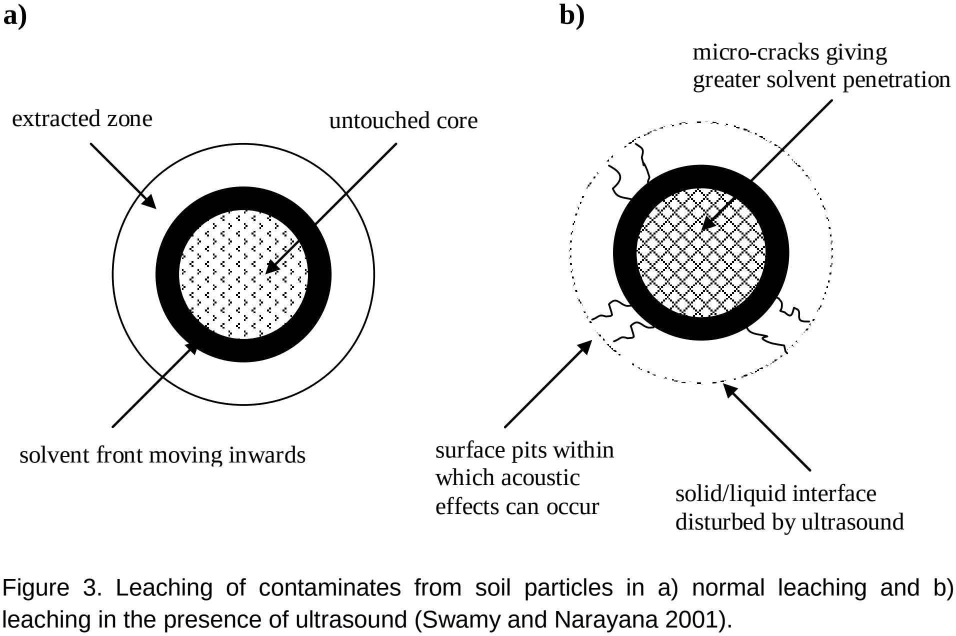


Figure 3. Leaching of contaminates from soil particles in a) normal leaching and b) leaching in the presence of ultrasound (Swamy and Narayana 2001).

Normal leaching takes place as the solvent front moves inward and steady-state diffusion occurs through the deplented outer region at a rate of equal to the reaction within the reaction zone itself (Fig. 3a). Under the influence of ultrasound normal leaching occurs but several additional factors contribute to improvements in its efficiency (Fig. 3b). These phenomena have also been summarized by Mason (2002):

1. Asymmetric cavitation bubble collapse in the vicinity of the solid surface leading to the formation of high-speed micro jets targeted at the solid surface. The micro jets can enhance transport rates and also increase surface area through surface pitting.
2. Particle fragmentation through collisions will increase surface area.
3. Cavitation collapse will generate shock waves, which can cause particle cracking through which the leaching agent can enter the interior of the particle by capillary action.
4. Acoustic streaming leading to the disturbance of the diffusion layer on the surface.
5. Diffusion through pores to the reaction zone will be enhanced by the ultrasonic capillary effect.

6.2 Ultrasound-assisted surface cleaning of particles, leaching of pollutants, and extraction of contaminated soil

Newman *et al.* (1997) compared the efficiency of conventional and ultrasonically assisted pollutant extraction procedures using model soil samples (granular pieces of brick) which had been deliberately contaminated with 51 ppm of copper (oxide). Analysis of the brick particles after 30 minutes' sonication (washing by passing water across the substrate on an ultrasonically shaken tray) revealed that the average copper content had fallen to 31 ppm, a reduction of about 40%. Using a conventional mechanical shaking tray for the same time period, the residual contamination was 48 ppm, which represented a reduction of only 6%. The majority of the copper was removed as a result of the removal of surface materials which were more heavily contaminated with the copper oxide.

Mason (2000) reported that the disposal of drilling mud represents an environmental problem on offshore oil drilling rigs. This material is a complex mixture of components which is injected into the drill hole as a lubricant and flotation agent. After it has been used, the mud, together with earth from the drill hole, is contamined with oil which must be throughtly removed before the solids are dumped to the sea. Cleaning methods exist for this, but the cleaned material is then in the form of small agglomerates which, when dumped in the sea, sink to the sea bed and accumulate around the platform legs. This represents a problem for sea life and a hindrance to rig maintenance. An ultrasonic device has been built to de-agglomerate the cleaned mud on-site, *i.e.* on the rig. The equipment provides flow treatment of the drilling mud, which substantially reduces particle size. As a result, when the mud is jettisoned from the oil rig it disperses across the sea bed and does not accumulate around the platform legs.

The list of sites contamined with toxic metals grows longer every year, presenting a serious health problem and a formidable danger to the environment. Therefore, the determination of metals and their impact on the environment have been studied comprehensively in recent years. Marín *et al.* (2001) studied an ultrasonically assisted extraction method (probe sonicator) for zinc and arsenic using soil samples. They reported that it is possible to assist conventional extraction with mechanical shaking by sonication in order to simplify analytical procedures, which is very necessary when many samples have to be tested.

Kim and Wang (2003) reported the effectiveness of ultrasound enhancement in the insitu soil-flushing remediation method of soil contamined by non-aqueous phase liquid hydrocarbons. A range of conditions involving soil type, soil density, flushing rate, and sonication power were studied. The test results indicated that sonication can enhance pollutant removal considerably, and that the degree of enhancement depends on a number of factors such as sonication power, water flow rate, and soil type. For example, increasing sonication power will increase pollutant extraction only up to the level where cavitation occurs and the effeciveness of sonication decreases with flushing rate but eventually becomes constant under higher flow rates.

Nitrated polycyclic aromatic hydrocarbons are widespread environmental pollutants. A number of them have proved to be mutagenic and carcinogenic. Polynuclear aromatic hydrocarbons (PAH) can undergo atmospheric reactions with nitrogen oxides to form nitro derivates but nitrated polycyclic aromatic hydrocarbons can also be directly emitted by diesel and petrol engines. Priego-López and Luque de Castro (2003) performed studies using continuous ultrasound-assisted extraction (20 kHz; 100 W) of nitrated polycyclic aromatic hydrocarbons from soil prior to their individual separation and determination. The use of a dynamic approach allowed the extraction of the analytes in 10 min versus 24 h for the reference method and the use of less than 10 mL of axtractant versus 100 mL with the reference method. Moreover, similar extraction efficiency for all the analytes in natural contaminated soils was obtained by the proposed method in comparison to the reference method.

The ultrasound remediation process has proved to be particularly efficient for the removal and destruction of polychlorinated biphenyl (PCB) contaminants in soils (Mason *et al.* 2004). The process was also recently demonstrated in treatability-scale studies for the remediation of tar ponds (Mason 2007b). The tar ponds region is one of Canada’s most contamined sites and includes PCB and PAH contamination as a result of industrial waste being dumped into an estuary over many years. Initial trials appeared very promising in that soil samples mixed to provide a uniform sample of 160 mg/kg PCB and 9.7–470 mg/kg of 19 different PAH can be cleaned to acceptable environmental standards.

Mason *et al.* (2004) reported that Australia suffers from soil pollution as do many developed countries and a research group in New South Wales has run a project in which ultrasound is used to enhance the rate of clean-up of soils. Among the range of pollutants investigated were insecticides and polycyclic aromatic compounds. Laboratory studies have been conducted to remove various contaminants from soils. Most were carried out with slurries using a 12.5 mm tip diameter Misonix horn delivering approximately 170 W. Pure 4,4'-(2,2,2-trichloroethane-1,1-diyl)bis(chlorobenzene) (DDT) and PCB Aroclor 1260 were dissolved in acetone diluted with water and added to washed, fine sand (effectively pure SiO_2). This was tumbled and allowed to dry to ensure even adsorption onto the sand surface. Fifty weight percent aqueous sand slurries were then made up. After sonication, the liquid was decanted and the soil was dried. The samples were then subjected to conventional extraction in order to determine the residual contaminant levels using a gas chromatograph combined with a mass spectrometer (GC-MS). The results showed that DDT reduction after 10 min ultrasound treatment was 70% and after 60 min about 75%. In the case of PCB the reduction after 10 min was about 50%, but after 60 min treatment even 85%. The study was extended to the decontamination of sediment at an industrial site polluted with PAH (containing at least 15 compounds). The sediment, with an original contamination of approximately 400 ppm, was made up to 44.4 wt% with distilled water and then sonicated as above. The results show that the reduction of industrial PAH compounds after 5 min ultrasound treatment was 75%.

Sanz *et al.* (2005) reported that nowadays it has become clear that the mobility, bioavailability, stability, retention, and toxicity of trace elements depend on both the chemical from which they enter the system and the final form in which they are present. Thus, the assessment of environmental impact and risk to human health must be based on the identification and quantification of the different chemical forms of the elements. For example, in the case of arsenic, the inorganic forms arsenite and arsenate have been related to an increased risk of cancer as well as to cardiovascular diseases, whereas methylated forms of arsenic are significantly less toxic. Arsenic speciation analysis suffers in general from the high sample handling time required by sample preparation. Sanz *et al.* (2005) reported a method of arsenic extraction from soil samples using a sonotrode-type ultrasonic homogenizer. They found that ultrasound sonication is a powerful tool for sample treatment allowing, in most cases, quantitative extraction in a very short time (from hours to a few minutes) compared to other methods, also simplifying sample handling.

Collings *et al.* (2006) reported processing contamined soils and sediments using high-power ultrasound on three scales: (i) a small laboratory scale (150 W); (ii) a larger scale (1–1.5 kW); and (iii) a 4 kW pilot plant. A significant improvement in the rate and completeness of destruction was achieved by ensuring that all the contaminated soil passes through the zone of most intense cavitation. Ninety precent of the PCB was reduced in 1–2 min and 99% in 7–10 min of sonication. Similar results were obtained for slurries contamined with hexachlorobenzene. In the larger-scale studies using contamined soil from an industrial site, where a mixture of organochlorine compounds, petroleum hudrocarbons, and PAH were present, ultrasound was effective in destroying the major contaminants: atrazine, simazine, and total petroleum hudrocarbons.

Richter *et al.* (2006) studied the efficiency of extraction of aliphatic diesel range organics and PAH from soil using ultrasound-assisted pressurized solvent extraction. They found that ultrasound improves extraction efficiency considerably. Under the conditions used (ultrasonic water bath at 70 °C; 35 kHz), the extraction time can be reduced by half compared with pressurized solvent extraction without ultrasound assistance.

Väisänen and Iljander (2006) optimized the method of ultrasound-assisted extraction followed by inductively coupled plasma optical emission spectrometry for the determination of trace element concentrations (arsenic, copper, lead, antimony, and zinc) in shooting range areas. Ultrasound extraction was performed using an ultrasonic water bath (35 kHz, 650 W). The optimized sonication procedure for a 500 mg soil sample lasted 9 min and was carried out at a temperature of about 50 °C. The sonication procedure was divided into three equal steps with the sample bottle being shaken by hand between each step. The shaking was used to prevent sedimentation. After ultrasound-assisted extraction the sample solution was filtered, washed, diluted, and analyzed.

Elik (2007) reported that the contamination of sediments, soils, and biota by heavy metals is of major concern in many industrialized countries because of their toxicity, persistence, and bio-accumulative nature. Elik (2007) studied the effect of ultrasound on the leaching of trace metals from sediments as a function of pH. He leached Cu, Pb, Ni, Zn, and Mn from sediments by ultrasound using phthalate buffers at pH values of 2.2–6.0. The ultrasonically assisted leaching method reduces the time required approximately from 12 h to 25 min compared to the conventional method. Depending on the metal and sample type, metal removal increased linearly or exponentially with decreasing pH. Elik (2007) summarized that it is clear that the ultrasonically assisted leaching method is a rapid, inexpensive, reproducible, and selective technique for the determination as a function of pH of Cu, Pb, Ni, Zn, and Mn in sediment samples which are important in monitoring environmental pollution. This technique is promising for the study of chemical and biological availability and uptake/release processes of metals in sediments and soil as a function of pH.

Song *et al.* (2007) also studied ultrasound-assisted extraction using soil samples. They reported that in recent years there has been a growing interest in the extraction of PAH from environmental soil samples due to risks of them causing adverse effects to human health. The conventional sample extraction methods have some drawbacks, such as long extraction time, large amount of organic solvents, labor-intensive procedures, and/or poor reproducibility. Therefore, some new extraction techniques like ultrasound-assisted extraction have been developed. Song *et al.* (2007) used an ultrasound cleaning bath in their ultrasound-assisted extractions. The soil sample was first irradiated then centrifuged, filtered, and analyzed using fluorescence analysis. Comparing the three extraction methods studied (ultrasound-assisted, microwave-assisted, and accelerated solvent extraction) the highest percentage recovery can be obtained using acclerated solvent extraction, but ultrasound-assisted extraction also gave better results than the conventional extraction methods.

Wang *et al.* (2008) performed experiments on the removal of organic matter and ammonia nitrogen from landfill leachate by ultrasound irradiation. The effects on COD reduction and ammonia removal of power input, initial concentration, initial pH, and aeration were studied. With increasing power input, the efficiency of COD removal was also increased. Initial COD concentration clearly affects the COD reduction efficiency. A lower initial COD concentration contributes to an increase in COD reduction efficiency. It is possible that organic matter with a lower initial COD concentration is more likely to enter the bubbles or encounter HO• radicals, while the gross COD reduction at a higher initial COD concentration is more than that with a lower initial COD concentration. COD reduction efficiency increased with increasing initial pH, but the effect of the initial pH was relatively small. Ultrasonic irradiation was shown to be an effective method for the removal of ammonia nitrogen from landfill leachate too. With increasing power input, the removal efficiency was increased and after 180 min ultrasound irradiation (20 kHz, 150 W), up to 96% ammonia-nitrogen removal efficiency can be achieved. The initial ammonia-nitrogen concentration has limited impact on removal efficiency, but increasing initial pH and aeration may enhance the sonochemical removal of ammonia-nitrogen in landfill leachate. Wang *et al.* (2008) concluded that the main mechanism of ammonia-nitrogen removal by ultrasound irradiation appears to be that the ammonia molecules in the leachate enter into the cavitation bubble and transform into nitrogen and hydrogen molecules via pyrolysis under instant high temperature and high pressure in the cavitation bubbles.

Much wastewater generated in agriculture, from chemical plants or in ground water leaching from fields is contamined with toxic and hazardous organic chloride compounds such as pesticides and herbicides. In Japan (4-chloro-2-methylphenoxy)acetic acid is one of the commonly used herbicides in rice fields. Compared to other pesticides and herbicides it is known to have higher toxicity and solubility in water. Ueno *et al.* (2009) reported an ultrasound-assisted extraction and decomposition method for (4-chloro-2-methylphenoxy)acetic acid in a model soil sample. In their studies the ultrasound frequency was 527 kHz and the ultrasound power 21 W. As a result, it was found that ultrasound irradiation significantly enhances (4-chloro-2-methylphenoxy)acetic acid extraction from model soil, which was attributed to various effects such as the formation of high-speed micro jets, particle fragmentation, and acoustic streaming on the disturbance of the diffusion layer on the surface.

7. Materials and methods

7.1 Ultrasound assisted polymer degradation (I → III)

7.1.1 Ultrasound equipment

In the polymer degradation studies three different ultrasonic reactors operating at 20, 40, and 900 kHz were used (Fig. 4). All the reactors were made by VTT. The volume of all the reactors was 10 L. The 20 and 40 kHz round-shaped reactors were made of steel. The rectangular-shaped 900 kHz reactor was made of plastic. The 20 kHz reactor had five and the 40 kHz reactor seven Langevin-type transducers installed on the bottom of the reactor. The surface of the 900 kHz transducer formed the entire bottom of the rectangular-shaped reactor. Ultrasonic frequency and power were adjusted using an ENI 1140 LA (S/N 563) power amplifier and a Tabor 8553 function generator or an IEC US1200 ultrasonic generator. The 900 kHz reactor had its own generator Megasonic 600.

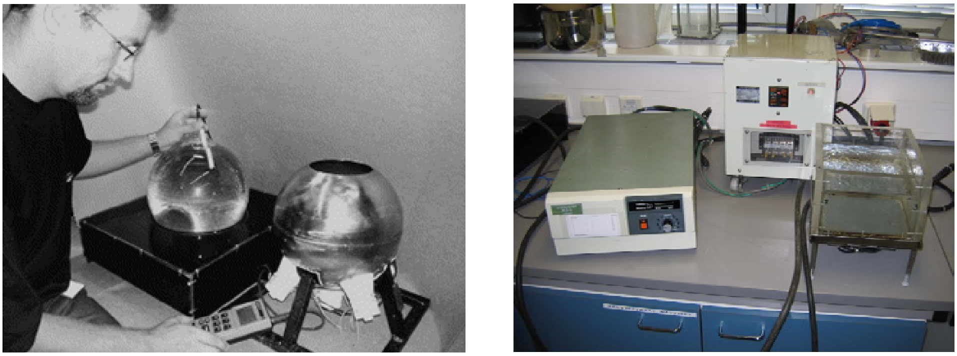


Figure 4. 20 kHz (left) and 900 kHz (right) ultrasonic reactors used in this study.

Calibration of the reactors was performed using hydrophone measurements. Hydrophone measurements also show the intensity of ultrasonic power.

7.1.2 Degradation methods

7.1.2.1 Polyvinyl alcohol

In the polyvinyl alcohol (PVA) studies, PVA obtained from BDH (British Drug House) laboratory supplies (average molecular mass 115,000 g/mol) was used to prepare PVA solutions at three concentrations (1%, 2%, and 3% (w/w)) with a mass of 5,000 g. No purification of the commercial PVA was performed and the ultrasonic treatments were performed at room temperature. Initially, the effect of ultrasonic input power on depolymerization, *i.e.* degradation of polymer was studied, and after that the depolymerization experiments were performed at two different ultrasonic input powers, one below and another above the cavitation threshold. It was quite difficult to measure the cavitation threshold but it was known that in water when the ultrasonic frequency is 20 kHz the threshold is in the range of 0.4–4.0 W/cm^2 depending on the air content of the water (Mason and Lorimer 1988). The measured viscosities of the PVA were only slightly higher than the viscosity of water and thus the cavitation threshold of PVA should be approximately equal to that of water. The hydrophone measurements showed that when using ultrasonic input power of 10 W (2 W/L) the ultrasonic intensities in the middle of reactor were 0.0–3.2 W/cm^2, and when using input power of 200 W (40 W/L) the ultrasonic intensities were 6.4–11.4 W/cm^2 (calculated by means of equations (14)–(17)). For this reason, the input power below the cavitation threshold used at 20 and 40 kHz was 10 W and above cavitation threshold 200 W. At 900 kHz, 120 and 600 W were used respectively. Each solution was irradiated for 2 h and the samples were withdrawn for analysis at 30, 60, 90, and 120 min. The dynamic viscosity of the PVA solutions before and after sonication was measured using a Haake VT 501 viscometer at room temperature.

7.1.2.2 Carboxymethylcellulose

In the carboxymethylcellulose (CMC) studies, nine CMC (CMC 1-CMC 9) samples obtained from CP-Kelco Oy were used. The initial RMM of the samples is shown in Table 2.

Table 2. The initial relative molecular mass (RMM) of the CMC samples.

Sample	**RMM, g/mol**
CMC 1	14,000
CMC 2	20,000
CMC 3	28,000
CMC 4	32,000
CMC 5	127,000
CMC 6	150,000
CMC 7	226,000
CMC 8	296,000
CMC 9	335,000

No purification of the commercial CMC samples was carried out. In these studies the ultrasonic input power was 80 W/L at 20 kHz, which were found to be the best sonication conditions for the polymer degradation studies in preliminary tests. The temperature of the ultrasonic reactor was adjusted to 40 ± 2 °C during sonication. Each solution was irradiated for 1 or 3 h. The samples in the 1 h cases were withdrawn for viscosity analysis at 0, 5, 15, 30, and 60 min and in the 3 h cases at 0, 5, 15, 30, 60, 90, 120, 150, and 180 min. The dynamic viscosity of the CMC solutions before and after sonication was measured at room temperature using a Haake VT 501 viscometer. The RMM measurements were obtained using a Waters 501 HPLC with a Waters 717 autosampler, a Jordi Gel GBR 500A column, and a Polymer Laboratories PL-ELS 1000 detector. In some CMC studies the initial viscosities of the samples were adjusted using polyethylene glycol (PEG). PEG was chosen for viscosity adjustment because it was not affected by ultrasonic irradiation when the temperature was adjusted. If the temperature was allowed to increase up to 70 °C caused by ultrasonic irradiation, other ultrasonically assisted reactions like polymerization of PEG took place and the dynamic viscosity of PEG increased (Fig. 5).

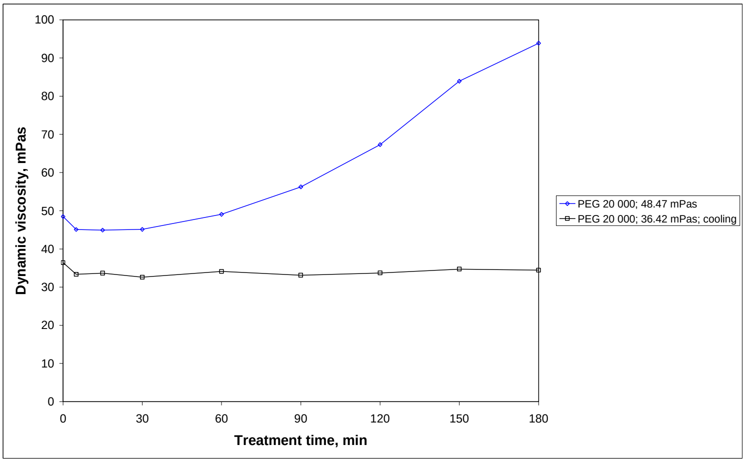


Figure 5. Ultrasonic degradation of PEG with and without cooling.

7.2 Disintegration of sewage sludge (IV)

7.2.1 Ultrasound equipment

Two kinds of ultrasonic reactors made by VTT Processes were used in sludge degradation. Most of the experiments were done with 10 L round steel batch reactors operating at 20 or 40 kHz frequencies. The reactors comprised a Tabor Electronics 8553 or AMREL Model FG-506 function generator, an ENI Model 1140LA-1331 power amplifier, and a IKA EUROSTAR digital lab mixer. The second ultrasonic device was a 27 kHz rectangular batch reactor with an IEC US-1200A ultrasonic generator. The volume of the second reactor could be changed (Fig. 6).

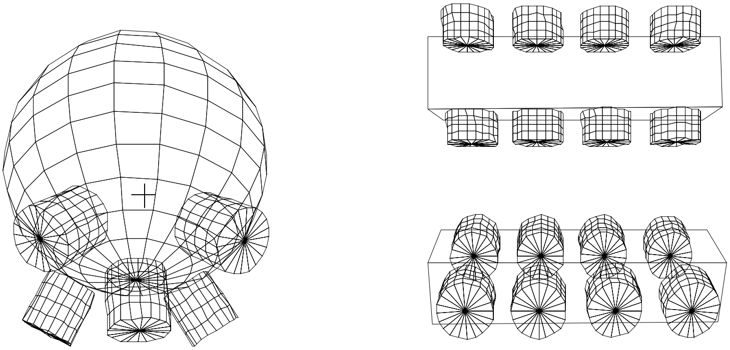


Figure 6. On the left the scheme of a round steel batch reactor with 5 Langevin-type transducers and on the right the scheme of a rectangular batch reactor with 8 Langevin-type transducers.

The ultrasound propagation studies were performed using a hydrophone (Reson 199010) and the visual effect of ultrasound was studied using aluminum foil. The propagation experiments were carried out in a rectangular batch reactor.

7.2.2 Sludge and methane production assays

Excess sludge from the Nenäinniemi wastewater treatment plant in Jyväskylä, Finland was used. The extent of cell disintegration of the excess sludge was determined as an increase of SCOD in the sludge supernatant. The supernatant for SCOD analyses before and after ultrasonic treatment of the sludge was obtained by high-speed centrifugation (30 min, 3023 *G*). Sludge samples were preserved using 4-M sulfuric acid before the SCOD analyses. The SCOD analyses were performed using a Hach DR/2000 spectrophotometer.

Methane production assays were performed at Jyväskylä University using 120 mL serum vials. After adding the inoculum (5 mL) and the studied material (20–30 mL), distilled water was added to obtain the final liquid volume of 60 mL. The inoculum was mesophilically digested sewage sludge (TS 2.2%, VS/TS 0.56) from the Nenäinniemi wastewater treatment plant. TS and VS were analyzed according to Finnish standards (SFS 3008). The pH of the inoculum and studied untreated and ultrasound treated sludge samples was 6.9–7.3. Vials with inoculum and without added material were assayed to subtract the methane produced by the inoculum from the studied sludge. The content of the vial was flushed with nitrogen to remove oxygen, and the vials were sealed with butyl rubber stoppers and aluminum crimps. The methane production assays were carried out over 19 days at 35 °C. A Perkin Elmer Autosystem XL gas chromatograph was used to determine the methane content of the biogas.

7.2.3 Oxidizing experiments

Oxidizing experiments were carried out in the 20 kHz round batch reactor with a mixer using peracetic acid (CH_3CO_3H) and hydrogen peroxide (H_2O_2) as oxidizing agents. The concentration of the peracetic acid was 38–40% and that of the hydrogen peroxide 50%. The amount of peracetic acid varied in the range 4–20 kg/t DS and that of hydrogen peroxide 25–70 kg/t DS. The incubation time varied from 10 to 20 min. The oxidizing agents were added to the sludge before, during or after ultrasound disintegration. The temperature before incubation of the oxidizing agents was 14 ± 2 °C. Pure oxidizing treatment increased the temperature by 3 °C while ultrasound treatment increased the temperature by 4–16 °C depending on the treatment time. SCOD and total organic carbon (TOC) were used to study the effect of oxidizing agents on disintegration of sludge. TOC analyses were performed using a Shimadzu TOC 5000A Total Organic Carbon Analyzer. Sample preparation for the TOC analyses was carried out using the same method as for the SCOD analyses except that the TOC samples were also filtered using GF50 filter paper.

7.2.4 Multivariate data analyses

The Unscrambler-multivariate data analysis program was used to study the effect of ultrasonic power, ultrasonic frequency, sludge DS, mixing of the sludge, temperature of the sludge, and ultrasonic treatment time on SCOD. The data collected were analysed with a “Projection to Latent Structures”-regression method (PLS), included in the Unscrambler software package made by Camo A/S in Norway, in order to generate a mathematical model for sludge dewatering. The model validity and the number of principal components were determined with the help of leverage correction method. The experiments were carried out in round batch reactors. A twofold factor method and a Box Behnken program were used to design the experiments and the PLS-1 method was used to analyze the results. SCOD was the response variable in both cases.

7.3 Remediation of contaminated soil (V)

7.3.1 Ultrasound equipment

A round-shaped 10 L ultrasonic reactor with five 20 kHz piezoceramic transducers on the bottom of the reactor was used in each batch experiment. Ultrasonic frequency and power were adjusted using an ENI 1140 LA (S/N 563) power amplifier and a Tabor 8552 function generator or an IEC US1200 ultrasonic generator. An input power of 100 W up to 500 W was used in the experiments. The effect of different treatment time and ultrasound pulsation on the remediation of different soil fractions was studied. The soil was diluted with water for the experiments and mixed during ultrasonic treatment using agitator rotations of 150–200 per minute. All the experiments performed are shown in Table 3.

Table 3. Conditions of ultrasonic treatment in remediation of contaminated soils.

Experiment	**Soil/kg**	**Water/kg**	**Power/W**	**Treatment time/min**	**Pulsation (on/off 0.5 s)**
Exp 1	1	5	250	60	No
Exp 2	1	5	500	30	No
Exp 3	1	5	-	-	-
1	0.75	1.25	250	60	No
2	0.75	1.25	250	15	No
3	0.75	1.25	250	5	No
4	0.75	1.25	-	-	-
5–6	0.75	1.25	250	30	No
7	0.75	1.25	250	15	No
8	0.75	1.25	250	15	No
9	0.75	1.25	-	-	-
11**	0.35	2	250	15	No
12**	0.4	2	250	15	No
13	0.58	1.74	100	5	No
14	0.58	1.74	100	5	Yes
15	0.58	1.74	100	0.5	No
16	0.58	1.74	250	5	No
17	0.58	1.74	250	5	Yes
18	0.58	1.74	250	2.5	No
19	0.58	1.74	250	0.5	No
20	0.58*	1.74	400	5	Yes
21	0.58	1.74	-	-	-
22	0.58	1.74	250	5	No
23	0.58	1.74	250	5	No
24	0.58	1.74	-	-	-
25	0.29	1.74	250	2.5	No
26	0.58	1.74	-	-	-

*Sludge mass was 2.524 kg, ** not analyzed (NA)

7.3.2 The soil samples

The soil examined came from a former military shooting range. The coarsest material (> 20 mm), which did not contain bullets or parts thereof, was screened out before the ultrasonic treatment experiments. The other screen fractions – 20 mm ↔ 4 mm, 4 mm ↔ 1 mm, < 1 mm and < 250 µm containing heavy metals – were treated separately in a remediation process, now using ultrasound treatment before separations.

The contaminated soil fractions of 20 mm ↔ 4 mm and 4 mm ↔ 1 mm were treated separately using ultrasound before heavy medium separation tests. Reference tests for each test were made using the same procedure without ultrasound. The sink and float fractions from the heavy medium separation were analyzed using the XRF method. The laboratory-scale apparatus used in the heavy medium tests, Erickson's cones, is presented in Fig. 7. The density of the heavy medium used in the tests was 3.1–3.2 kg/dm^3 and the suspension was prepared by mixing water and ferrosilicon. In these conditions the stones could be recovered into the float product and the bullets and broken parts thereof into the sink product when the heavy medium was circulated by pumping. Contaminated soil was fed into the upper cone. The tests were carried out as batch experiments.

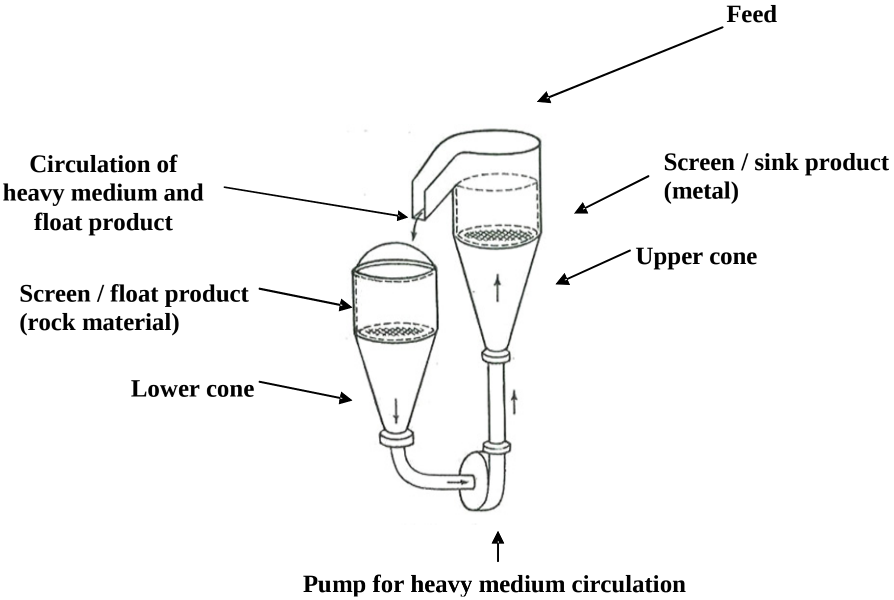


Figure 7. Laboratory-scale apparatus (Erickson's cones) for heavy medium separation.

The ultrasonically treated < 1 mm fraction was screened into eight smaller fractions and the metal content (lead and copper) in each fraction was analyzed using the XRF method.

The < 1 mm fraction was first screened into fractions of > 250 and < 250 μm before flotation and US treatment. Flotation experiments were performed only for the < 250 μm fraction because the flotation method used could not effectively operate with > 250 μm particles. This shortcoming will be avoided in the follow-up study by using SIF (flotation in froth) technology, which can operate with < 1 mm material. The < 250 μm soil fraction was first treated using ultrasound with different combinations of treatment time and pulsation, and then floated. The mineral concentrates and tailings from the flotation were filtrated and the metal contents (lead and copper) were analyzed using the XRF method on the filter cakes. The flotation experiments were mainly carried out using a turnip fatty acid-type collector (RaRa). Emulgator-type KOAL 10 was used to disperse the fatty acid collector in the water to improve the collection of hydrophobic particles. The sulfide collector potassium amyl xanthate (KAX) was used in some experiments alone or together with copper sulfate ($CuSO_4$) activator. The purpose of this activator was to alter the particle surface properties by changing, for example, the original Pb compound to the corresponding Cu compound to improve collection of particles better. NaHS activator was also used in some experiments together with the sulfide collector sodium isopropylxanthate (NaIPX). The purpose of the NaHS treatment was to modify the surface of the particles to be flotated to the corresponding heavy metal sulfides since in the latter state they can be more easily flotated than in their original form of heavy metal carbonate or pure heavy metal. NaOH (fatty acid flotation) and H_2SO_4 (xanthate flotation) were used for pH regulation.

8. Results and discussion

8.1 Degradation of polymer (I → III)

8.1.1 Effects of the main ultrasound parameters

8.1.1.1 Frequency of ultrasound

When using an ultrasonic input power above the cavitation threshold, the highest intensity value at 20 kHz, according to hydrophone measurements, was 9.5 W/cm^2, at 40 kHz 11.4 W/cm^2, and at 900 kHz 2.8 W/cm^2. Figure 8 shows the map of the hydrophone measurements of the reactor when operating at 20 kHz at 200 W.

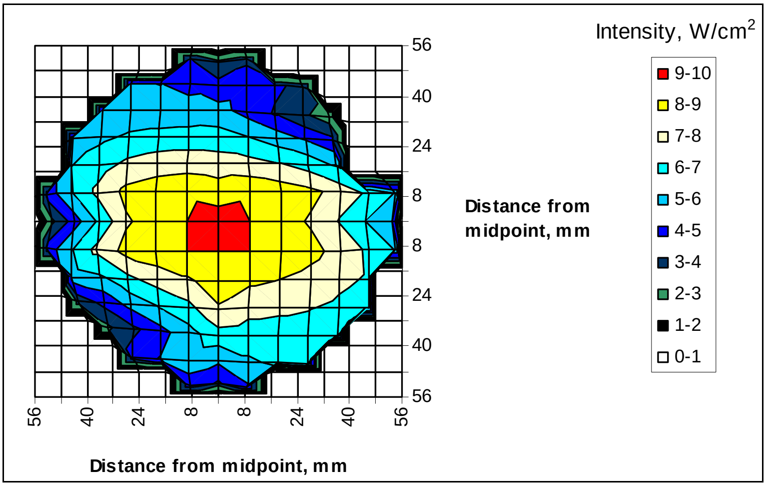


Figure 8. Hydrophone measurements of the reactor operating at 20 kHz. The ultrasonic input power was 200 W, the volume of water was 5 L, and the hydrophone was 6 cm from the bottom of the reactor.

Although the highest hydrophone values were reached using 40 kHz frequency, the most extensive degradation took place at the lowest ultrasonic frequency of 20 kHz (Table 4). Certainly the higher the applied frequency, the shorter the period for cavitation bubbles to grow and collapse, and the smaller the amount of time available to produce cavitation. As the frequency of the wave decreases, the shear forces are complemented by the increased cavitational effects. This study confirmed the general conclusion that the higher the irradiation frequency the lower the degradation rate is (Mason and Lorimer 1988, Price *et al.* 1994, and Portenlänger and Heusinger 1997).

Table 4. Changes in the dynamic viscosity of PVA after 2 h ultrasonication at different concentrations subject to different ultrasonic frequencies with an ultrasonic input power above the cavitation threshold.

PVA concentration, % (w/w)	**Dynamic viscosity, percentage of the initial value**		
	20 kHz, 200 W	**40 kHz, 200 W**	**900 kHz, 600 W**
1	85	84	77
2	71	75	86
3	69	80	86

8.1.1.2 Intensity of ultrasound

It was found that depolymerization requires the power to exceed the cavitation threshold, which is in agreement with earlier studies (Mason and Lorimer 1988). When using PVA at an input power below the cavitation threshold only a slight decrease in viscosity was detected. Even in the best situation, when the hydrophone measurements indicated a slight cavitation in the hot points of the 20 kHz and 40 kHz reactors, the decrease in viscosity was only about 10% (Table 5).

Table 5. Changes in the dynamic viscosity of PVA after 2 h ultrasonication at different concentrations when the ultrasonic input power was below the cavitation threshold.

PVA concentration, % (w/w)	**Dynamic viscosity, percentage of the initial value**		
	20 kHz, 10 W	**40 kHz, 10 W**	**900 kHz, 120 W**
1	90	90	96
2	91	96	98
3	90	94	97

When the ultrasonic input power was above the cavitation threshold the decrease in viscosity was at least 14% and in the best situation 31% below the initial value (Table 6).

Table 6. Changes in the dynamic viscosity of PVA after 2 h ultrasonication at different concentrations when the ultrasonic input power was above the cavitation threshold.

PVA concentration, % (w/w)	**Dynamic viscosity, percentage of the initial value**		
	20 kHz, 200 W	**40 kHz, 200 W**	**900 kHz, 600 W**
1	85	84	77
2	71	75	86
3	69	80	86

Depolymerization studies using aqueous PVA showed that the viscosity decreased further when the ultrasonic input power was increased from 10 W to 100 W. From 100 W to 350 W the viscosity decreased less (Fig. 9). In the case of CMC it was found that degradation was at the same level after the input power was beyond 200 W. For this reason, there was an optimum input power for the degradation of polymers. One explanation for this behavior might be that when the input power was raised there was a point after which the cavitation bubbles stayed very near the transducer or reactor surface and did not proceed to the liquid at all. Another possible explanation is that at high input power the efficiency of sonochemical processes may be diminished, since the cavitation bubbles present at high concentration may scatter the ultrasound waves (Czechowska-Biskup *et al.* 2005). The optimum input power had to be below this point.

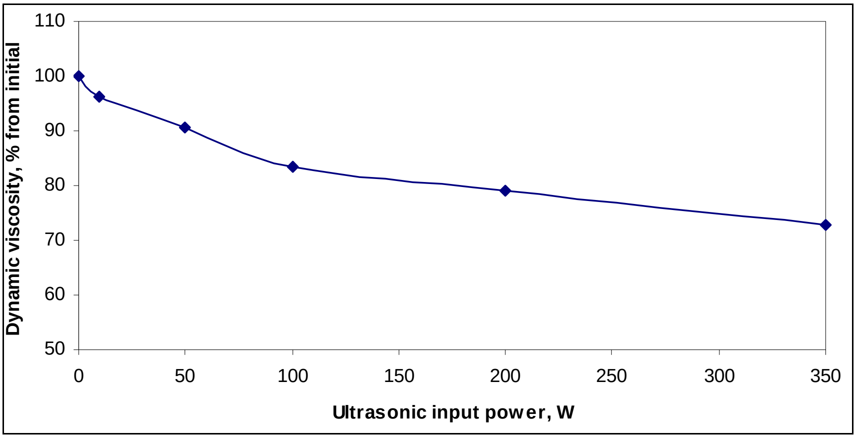


Figure 9. The change in dynamic viscosity as a function of ultrasonic input power using 2% PVA and a 20 kHz ultrasonic transducer.

8.1.1.3 Molecular mass and concentration of polymers

The biggest changes in dynamic viscosity when using PVA polymers were in the 3% (w/w) solution. Whereas, the greatest decrease in RMM occurred with a PVA concentration of 1% (w/w). RMMs were measured using viscosity calibration. The viscosity of three commercial PVA polymers with RMMs of 22,000 g/mol, 72,000 g/mol, and 115,000 g/mol was measured and used to draw a calibration curve (Fig. 10).

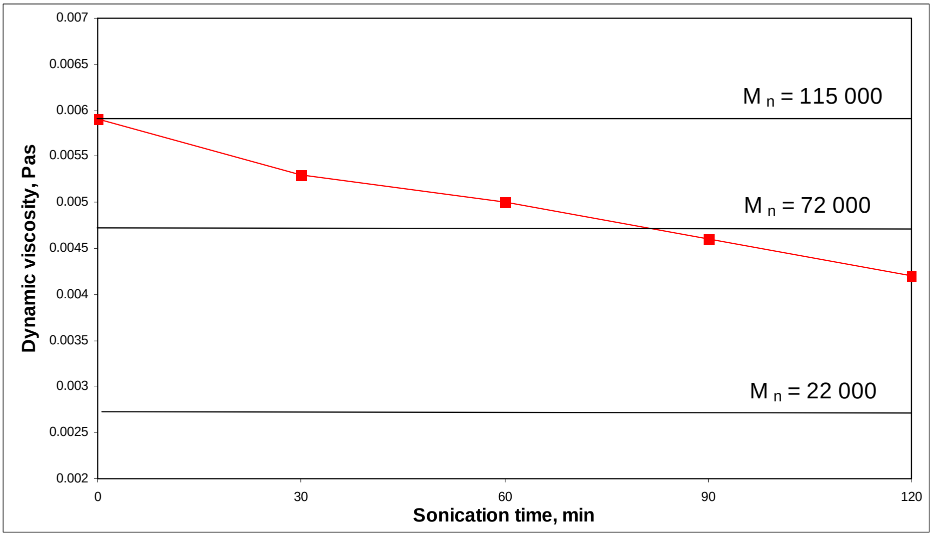


Figure 10. The viscosity calibration of 2% (w/w) PVA solution (20 kHz; 200 W).

Viscosity calibration showed that the RMM of PVA with a concentration 1% (w/w) was about 30,000 after sonication. In the case of PVA at concentrations of 2% and 3% (w/w), the RMMs were about 60,000 and 75,000 after sonication. This confirmed the general assumption that in each case the extent of degradation is found to decrease with an increase in solute concentration (Mason and Lorimer 1988, Kanwal *et al.* 2000, Xiuyuan *et al.* 2001, Trciński and Staszewska 2004, Waskiewicz *et al.* 2005, Petit *et al.* 2007, and Desai *et al.* 2008). However, in the case of CMC concentration studies using viscosity measurements showed that there was an optimum CMC concentration for the most efficient degradation (Fig. 11).

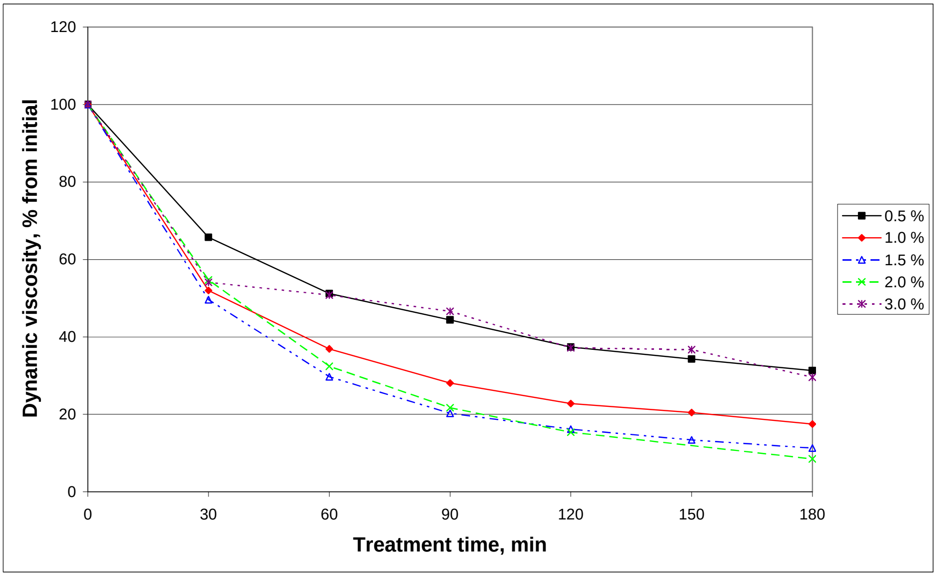


Figure 11. The effect of polymer concentration on the degradation of CMC 5.

Viscosity was dependent on the concentration of the polymer. When the concentration was smaller than the optimal concentration the shear forces due to low viscosity were not strong enough to cause efficient degradation. When the concentration was higher than the optimal concentration, the polymer molecules became less mobile in solution due to high viscosity and the velocity gradients around the collapsing bubbles became smaller. Thus, this study confirmed the general assumption that the shear forces generated by the rapid motion of the solvent are responsible for the breaking of the chemical bonds within the polymer.

The effect of initial RMM of all the nine CMC polymers on the degradation rate was studied for an initial concentration of 1.0% (w/w). The viscosity of those polymers with a large RMM decreased significantly. In contrast, the viscosity decrease of the polymers with a small RMM was minor. Thus the extent of ultrasonic depolymerization decreased with decreasing molecular mass of the polymer. The studies showed also that the degradation of molecules continued only to a certain limiting molecular mass. This was in agreement with the results obtained in earlier studies (Basedow and Ebert 1975, Mason and Lorimer 1988, Lorimer *et al.* 1995, Madras *et al.* 2000, Xiuyuan *et al.* 2001, Kuijpers *et al.* 2004, Li J. *et al.* 2004 and 2005, Li Y. *et al.* 2005, Waskiewicz *et al.* 2005, Vodeničarová *et al.* 2006, Petit *et al.* 2007, Desai *et al.* 2008, and Kobayashi *et al.* 2008). The molecular mass limit of the CMC polymer in viscosity units was about 0.0040 Pas. Below this limit, the polymer chain was so short that it followed ultrasonic vibration flexibly and cleavage at the centre of the molecule no longer took place.

The RMM studies above were undertaken using 1.0% (w/w) CMC 1–CMC 9 samples which had different initial viscosities. For example, Mason and Lorimer (1988) reported that viscosity has an influence on degradation. Hence the result of the RMM studies had to be verified using polymers with different RMMs but the same viscosity. The results showed that when the initial dynamic viscosities were adjusted to the same level using PEG, the higher the molecular mass of the polymer, the larger the change in dynamic viscosity was after 180 min, as can be seen in Fig. 12. For this reason, the verification studies gave similar results to those obtained when the samples had different initial viscosities.

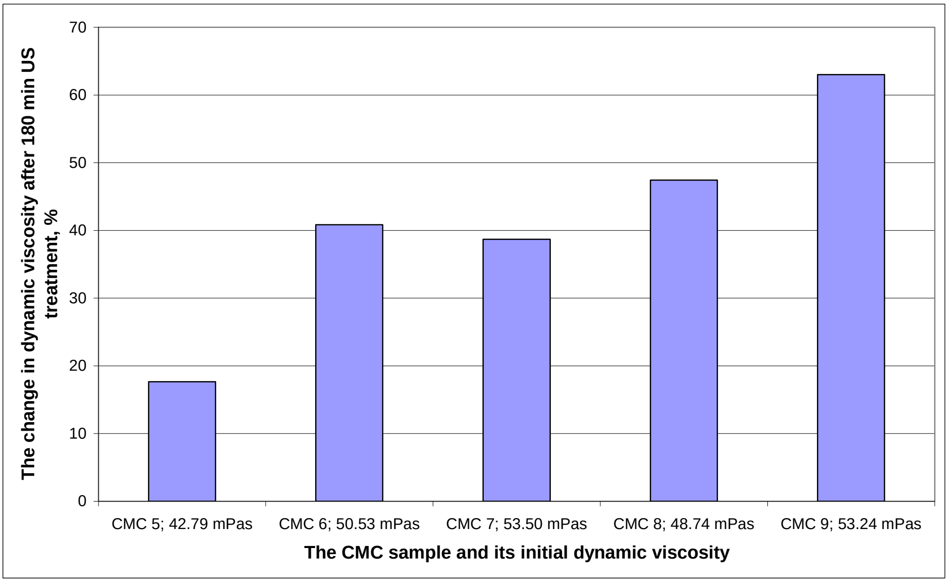


Figure 12. Effect of molecular mass on the change in dynamic viscosities of CMC polymers after 180 min ultrasound treatment when the initial dynamic viscosity levels were similar.

According to this investigation the extent of ultrasonic depolymerization increased with increasing molecular mass of the CMC polymer. This observation strengthened the claim that ultrasonic degradation, unlike chemical or thermal decomposition, is a non-random process with cleavage taking place roughly at the centre of the molecule and with larger molecules degrading the fastest.

In the cases where the initial dynamic viscosities of the polymer solutions were not the same, the sonolytic degradation of CMC polymer mainly depended on the initial viscosity. The higher viscosity, the faster the degradation was (Fig. 13).

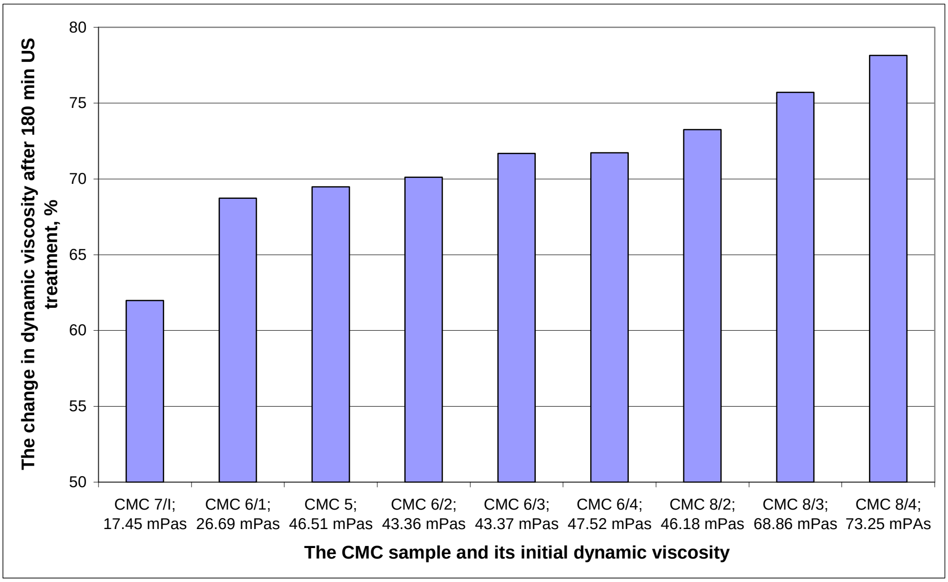


Figure 13. The effect of initial dynamic viscosities on the change in dynamic viscosities after 180 min ultrasound treatment.

The study also showed that in cases where the initial dynamic viscosities of the polymer solutions were not adjusted but the initial viscosities were almost the same, the longer the CMC polymer chain length the faster the degradation (in Figure 13; CMC 5, CMC 6/2, CMC 6/3, CMC 6/4, and CMC 8/2). This finding was also in agreement with earlier studies, where it has been suggested that the larger the molecule the faster the degradation (Basedow and Ebert 1975, Mason and Lorimer 1988, Lorimer *et al.* 1995, Madras *et al.* 2000, Xiuyuan *et al.* 2001, Kuijpers *et al.* 2004, Li J. *et al.* 2004 and 2005, Li Y. *et al.* 2005, Waskiewicz *et al.* 2005, Vodeničarová *et al.* 2006, Petit *et al.* 2007, Desai *et al.* 2008, and Kobayashi *et al.* 2008).

The CMC concentration studies proved that the higher the polymer concentration the higher the degradation rates when the initial viscosity was adjusted using PEG (Fig. 14). The changes in dynamic viscosity in Fig. 14 in the area of 0.25–1.00% w/w differed from the area of 1.25–3.00% w/w because of the different initial dynamic viscosity levels. This result was in disagreement with earlier results where degradation decreased with an increase in solute concentration (Mason and Lorimer 1988, Kanwal *et al.* 2000, Xiuyuan *et al.* 2001, Trciński and Staszewska 2004, Waskiewicz *et al.* 2005, Petit *et al.* 2007, and Desai *et al.* (2008). However, the result was in agreement with the ultrasound theory, because the effects resulting from the cavitation collapse in viscous liquids were stronger than the collapse in less viscous liquid. On the other hand, in those earlier studies mentioned above the viscosity was not adjusted, which according to this study is one of the main parameters in polymer degradation.

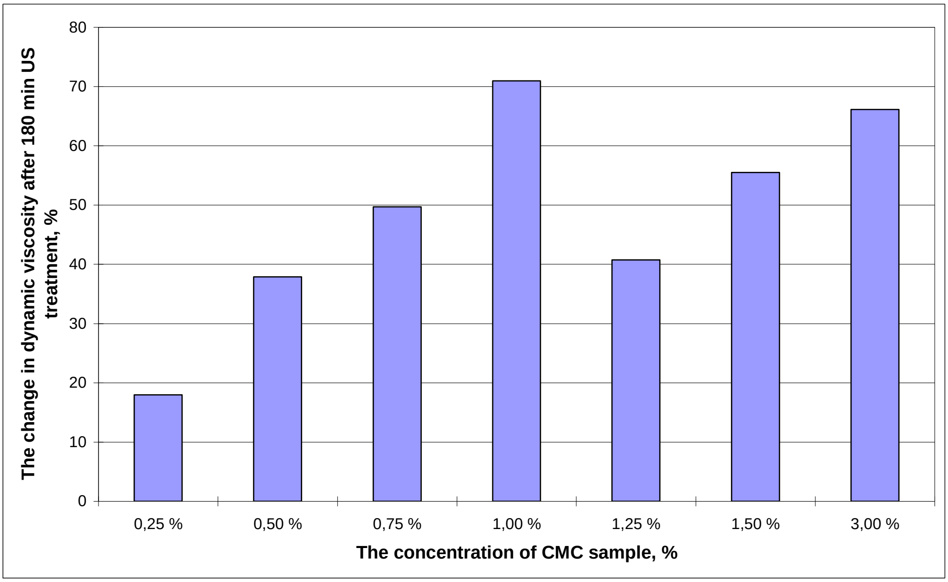


Figure 14. Effect of polymer concentration on the change in dynamic viscosity of CMC polymer mixtures after 180 min ultrasound treatment. The experiments were carried out at two viscosity levels (0.25–1.00% and 1.25–3.00%).

8.1.2 Degradation mechanisms

As metioned above, this study confirmed the general assumption that the shear forces generated by the rapid motion of the solvent are responsible for the breakage of the chemical bonds within the polymer. The rapid motion might be due to the high pressure shock waves associated with the collapse of cavitation bubbles or due to chemical reactions initiated by unstable intermediates. This study also indicated that ultrasonic degradation, unlike chemical or thermal decomposition, is a non-random process with cleavage taking place roughly at the centre of the molecule and with larger molecules degrading the fastest. It was found that the degradation of molecules continued only to a certain limiting molecular mass (Fig. 15).

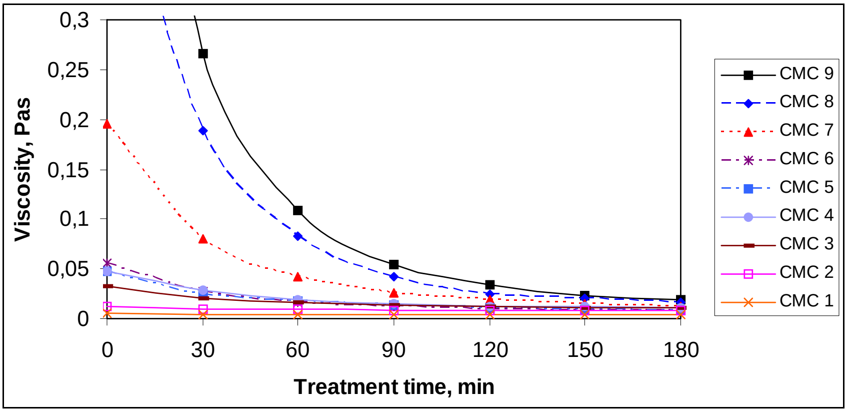


Figure 15. The viscosity of CMC samples as a function of depolymerization time.

8.2 Disintegration of sewage sludge (IV)

8.2.1 Multivariate data analysis and SCOD

Ultrasonic power, the dry solids (DS) of sludge, temperature of sludge, and ultrasonic treatment time (Tables 7 and 8) had an obvious effect on the disintegration of excess sludge. The largest SCOD increase was obtained with the highest power, highest DS, and longest treatment time used, which agreed with earlier studies (Quarmby *et al.* 1999, Schläfer *et al.* 2000 and 2002, Tiehm *et al.* 2001, Gonze *et al.* 2003, Wang *et al.* 2005, Dewil *et al.* 2006, Benedballah *et al.* 2007, Sehn *et al.* 2007, Show *et al.* 2007, Casellas *et al.* 2008, and Xie *et al.* 2009). This study indicated that also the temperature of sludge was an important parameter in ultrasonic disintegration, which also agreed with an earlier study (Shen *et al.* 2007).

Table 7. The effect of five different variables on SCOD when using the twofold factor method for experiment design and the PLS 1 method for result analyses.

Variable	Levels	SCOD
US power	100 or 200 W/L	++
US frequency	20 or 40 kHz	NS
DS of sludge	0.9 or 2.4%	++
Mixing of sludge	200 or 500 rpm	NS
Temperature of sludge	20 or 40 °C	++

NS = non significant meaning; − = the bigger value has a negative effect; + = the bigger value has a positive effect.

Table 8. The effect of three variables on SCOD when using the Box Behnkenprogram for experiment design and the PLS 1 method for result analyses.

Variable	Levels	SCOD
Treatment time (A)	5, 17.5 or 30 min	+++
US power (B)	50, 175 or 300 W/L	++
DS of sludge (C)	0.8, 1.6 or 2.5%	++
A and B together		++
A and C together		NS
B and C together		+

NS = non significant meaning; − = the bigger value has a negative effect; + = the bigger value has a positive effect.

The disintegration of sludge relied on the high mechanical shear forces caused by jet streams during cavitation bubble implosion. That was why disintegration requires high ultrasonic power. However, the optimization of energy consumption is essential in ultrasonic-assisted disintegration. Thus the joint effect of power and treatment time was studied further. A larger SCOD increase was obtained with the same energy consumption when using high ultrasonic power together with a short treatment time than when using low ultrasound power with a long treatment time (Fig. 16).

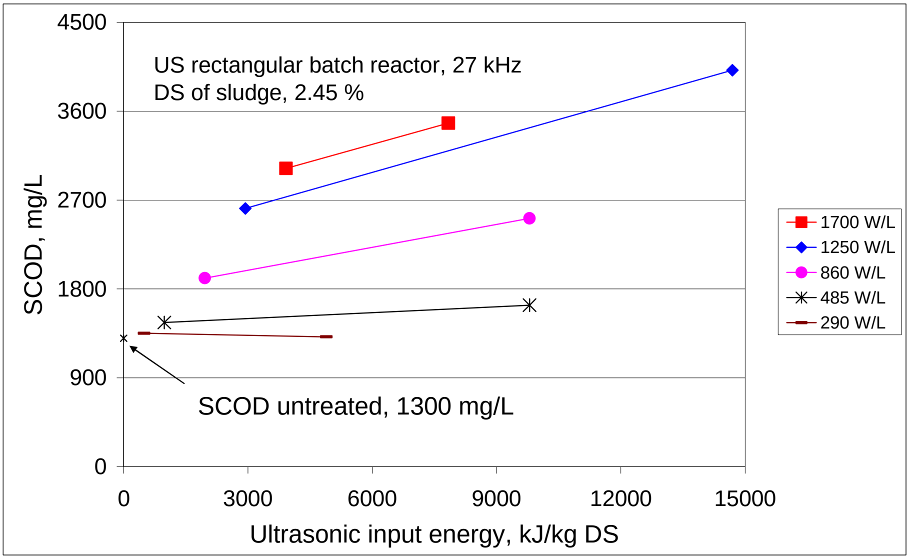
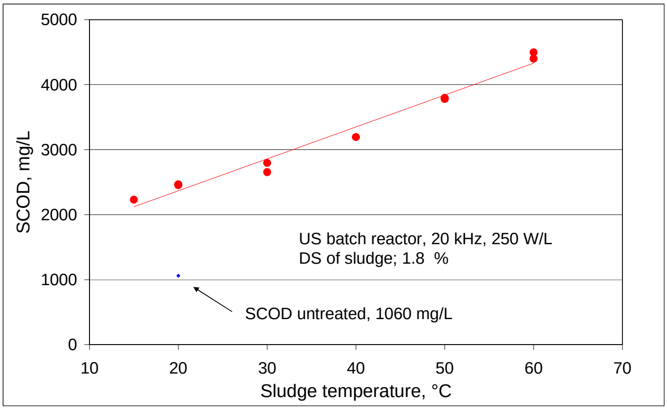


Figure 16. The effect of ultrasonic energy on SCOD when different ultrasonic efficiencies were used.

SCOD was observed to increase with sludge DS increase due to the higher concentration of microbes that could be disrupted. However, every ultrasonic reactor has a characteristic maximum DS enabling ultrasonic wave propagation and cell disintegration. The factors limiting this maximum DS value are, for example, reactor size, transducer type, viscosity of sludge, temperature of sludge, and polymer concentration if polymers are added in flocculation.

Multivariate data analysis showed that disintegration was enhanced with treatment temperature. In more accurate experiments, temperature was adjusted during treatment with and without ultrasound (Fig. 17). Heating increased the amount of SCOD. However, larger increases in SCOD were obtained with ultrasound than with heating alone.

a)



b)

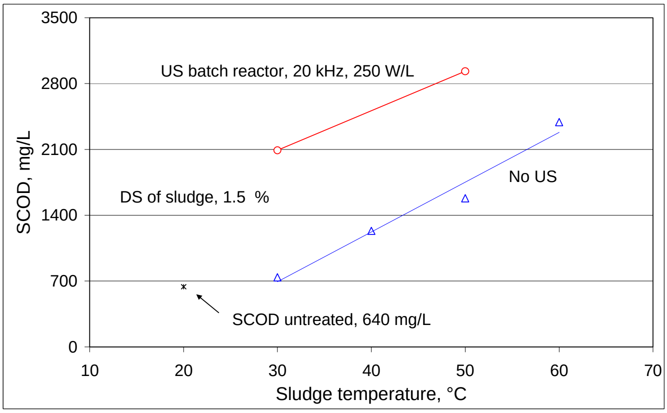


Figure 17. (a) SCOD values as a function of sludge temperature in experiments with ultrasound. (b) SCOD values at different sludge temperatures with and without ultrasound.

The ultrasonic frequencies and mixing rates used did not affect SCOD. However, the parameter values studied were so close to each other that the effects were not clear.

8.2.2 Effects on methane production

The effects of 2.5 and 10 min ultrasound treatment (20 kHz, 200 W/L) on the methane production of the filtrated fraction of excess sludge were studied in methane production assays using an untreated sample as a control. The longer the treatment time the higher the initial SCOD was in the beginning of the assays. With all the samples, methane production started without any delay. During the 19 days of assays, methane production was 8–17 times higher for the treated samples than for the untreated samples. Methane production per kilogram of SCOD in the sample was the same for the samples treated for 2.5 and 10 min, suggesting that the SCOD in these samples was equally degradable despite differences in the quantities of it (Table 9).

Table 9. The effects of ultrasound treatments on the SCOD of excess sludge and on the methane production of a filtrate of excess sludge in batch assays over 19 days.

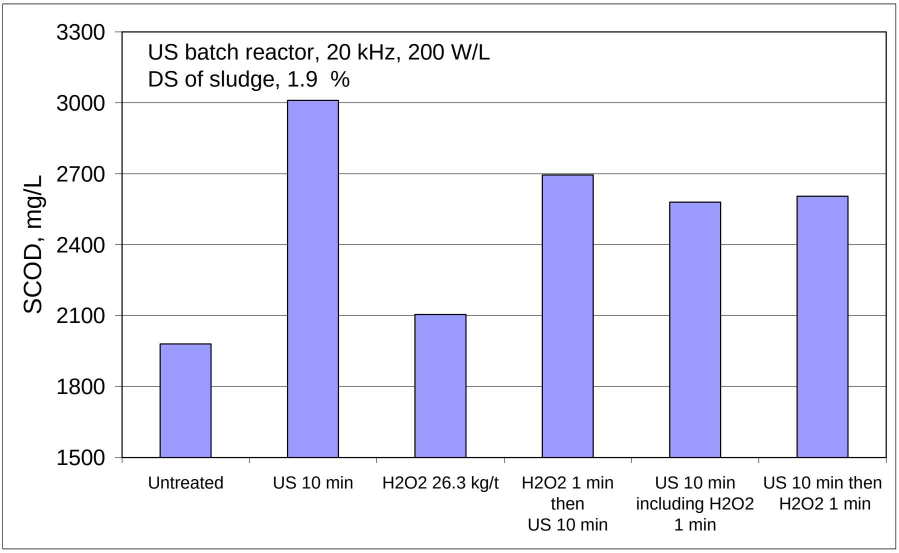
Sample	**SCOD, mg/L**	**Methane production, mL**	**Methane production, m^3/m^3 of sample**	**Methane production, m^3/kg SCOD in sample**
Untreated	620	2	0.07	3.22
2.5 min	2100	17	0.56	8.09
10 min	4200	34	1.13	8.09

Anaerobic batch studies were also performed with 20 differently treated samples of excess sludge. The ultrasound power ranged up to 300 W/L and the treatment times up to 30 min, while sludge TS ranged from 0.6% to 2.5%. The sludge used in the experiments was obtained from the plant using four different sampling times. The effects of various treatments on methane production varied without a clear trend. In some cases, the same treatment increased the methane production with one sample, but decreased with another. However, in most assays 10–20% more methane was obtained from treated sludge compared to untreated sludge. In general, the higher the SCOD after the treatment the more methane was produced. These results suggest that ultrasound treatment must be optimized separately in each application.

8.2.3 Oxidizing measurements

When studying the effect of peracetic acid or hydrogen peroxide on ultrasonically assisted sludge disintegration, the SCOD results showed that no increase in SCOD was achieved when using ultrasound together with oxidizing agents compared with ultrasonic treatment alone. There was no difference whether oxidising agents were added before, during or after ultrasonic treatment. Pure oxidizing agents had a slightly positive effect on SCOD but the effect was minor compared to that of ultrasonic treatment. When using oxidizing agents together with ultrasound, SCOD was even lower than when using ultrasound only (Fig. 18a). The result could not be improved by prolonging the incubation time or increasing the dosage of oxidizing agent in the circumstances studied. On the contrary, TOC results showed that peracetic acid has a slight effect on ultrasonically assisted sludge disintegration (Fig. 18b). However, no enhancement in methane production was noticed. When oxidizing agents disintegrated sludge, they at the same time destroyed the organic matter produced. This and perhaps the wrong oxidizing agent dosage might be the reason for a minor effect on the oxidizing results or methane production. The effect of the oxidizing agents on the sludge and ultrasonically assisted sludge disintegration is a complex phenomenon and needs further investigation.

a)



b)

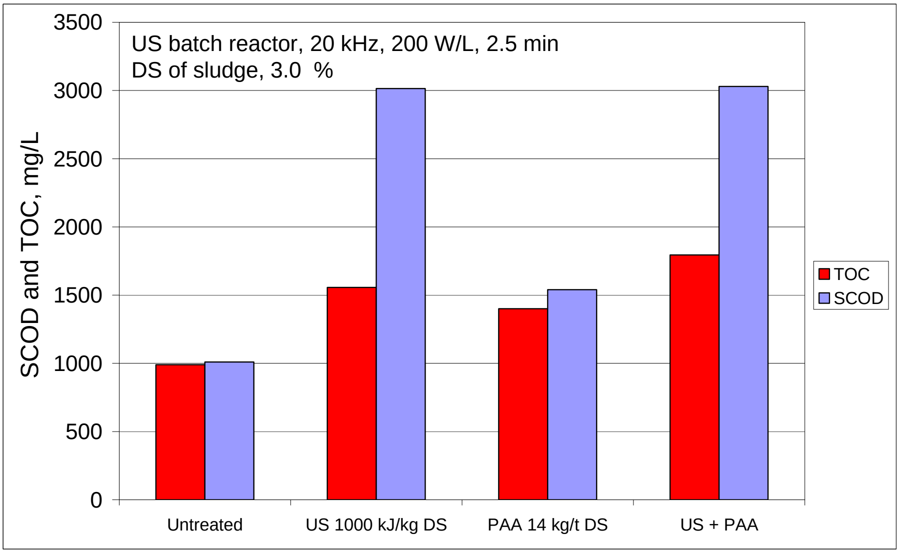


Figure 18. (a) SCOD content in sludge when using hydrogen peroxide as an oxidizing agent. (b) SCOD and TOC contents in sludge supernatants when using peracetic acid as an oxidizing agent.

8.2.4 Propagation of ultrasonic waves

It is important to be aware of the ultrasound propagated by the transducer when scaling up ultrasonic reactors. Ultrasonic propagation was measured using a hydrophone. The hydrophone value increased linearly as a function of ultrasonic input power at minor sludge thickness (DS 2.3%) in front of the transducer. When the sludge thickness was 4 cm or more, the hydrophone value even started to decrease when the input power exceeded 400 W due to poor ultrasound propagation (Fig. 19). When the ultrasonic power was high, cavitation bubbles appeared only in the vicinity of the transducer. This phenomenon also caused cavitation erosion at the transducer surface. Ultrasound propagation could be altered by sufficient mixing or flow. High power was found to disintegrate sludge efficiently. Thus input power and the propagation of ultrasound in sludge should be optimized when designing ultrasonic reactors for sludge disintegration.

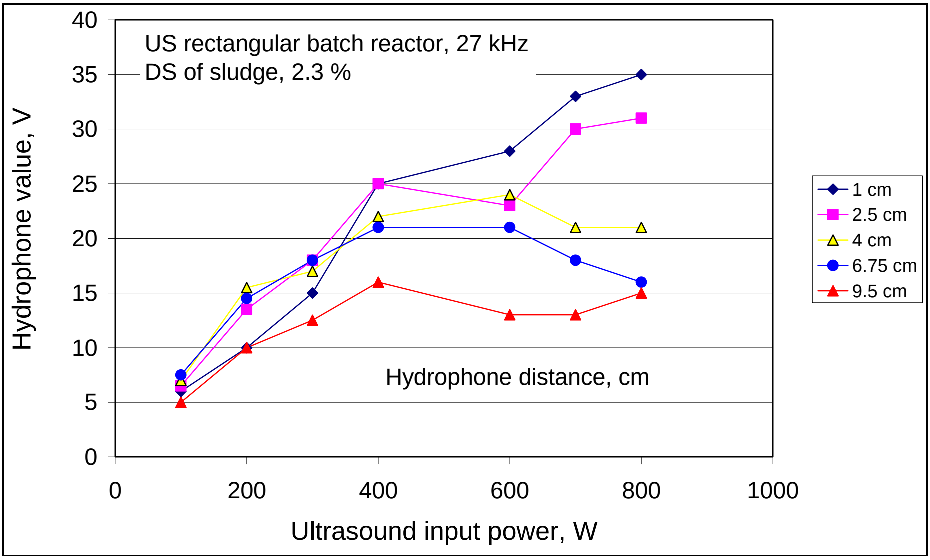


Figure 19. Studies of ultrasound propagation using a hydrophone.

The visual effect of ultrasound inside the rectangular reactor was also studied using aluminum foil. These experiments showed the periodic and local nature of ultrasonic cavitation. For example, more holes caused by cavitation formed on the aluminum foil when located at 13.5 cm rather than 6 cm from the transducer, while it was the opposite in the case of 14.5 cm and 5 cm (Fig. 20).

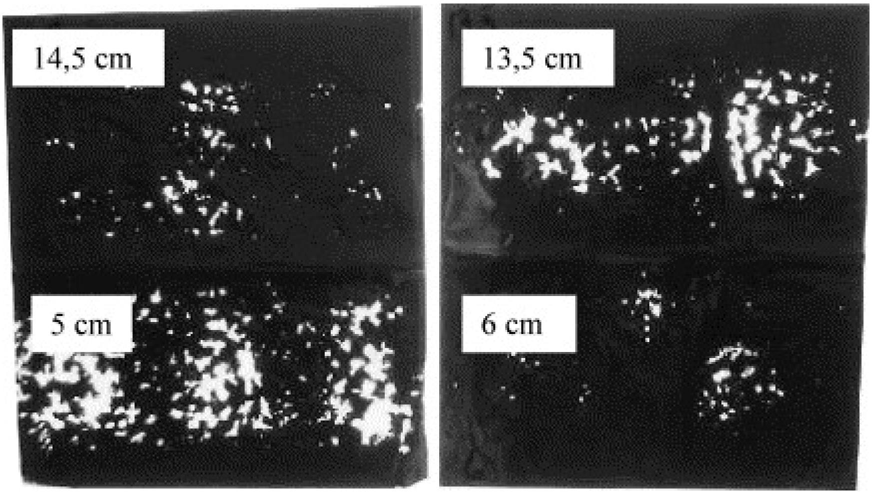


Figure 20. Visual studies of ultrasound using aluminum foil.

8.3 Remediation of contaminated soil (V)

8.3.1 Ultrasonic pre-treatment in heavy medium separation

In this study power ultrasound was used as an aiding method for the mineral processing technique, which has recently been developed for the remediation of soil contaminated by heavy metal containing bullets, broken parts thereof, and alteration products. Power ultrasound was used to disperse the soil to remove metals and metal compounds from soil particle surfaces instead of attrition conditioning. The effect of different ultrasonic powers, ultrasonic treatment times, and ultrasound pulsing were studied on the purity of sink and float fractions in the heavy medium separation process, on screen fractions, mineral concentrates, and tailings in the flotation process.

In heavy medium separation the ultrasonic pre-treatment experiments (experiments 1–3, Table 4) decreased the lead content in the float product of the 4 mm ↔ 1 mm fraction (rock material) from 0.47% at least to 0.15% (Fig. 21).

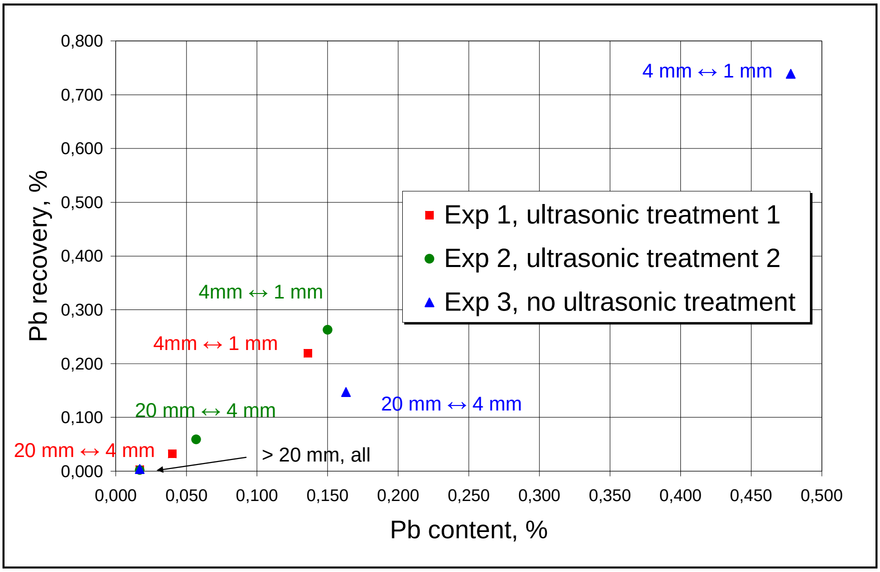


Figure 21. Results of heavy medium separation tests for different screen fractions.

Lead recovery into the same product decreased correspondingly from 0.75% to at least 0.3%. In the 20 mm ↔ 4 mm fraction the lead content decreased from 0.17% to at least 0.06%. The decrease in copper content was smaller in the remediated soil. A visual picture of the purification degree of the metal (sink) and rock material (float) fractions is given in Figure 22.

Figure 22. End products of sink-float process (left sink product, right float product).

The ultrasonic treatment of the fine test material (< 1 mm) (experiments 5–6, Table 4) caused a transition in the lead contents of the screen fractions. The treatment lowered the lead content in all the fractions apart from the finest (< 32 µm) fraction (Fig. 23). Copper content exhibited a trend similar to the lead content. The reason for this could be the accumulation of separated Pb and Cu in the finest fraction and ineffective US cleaning with this fraction. Swamy and Narayana (2001) performed CuO ore leaching experiments to show that 45 µm is the critical grain size, below which the application of US is not effective.

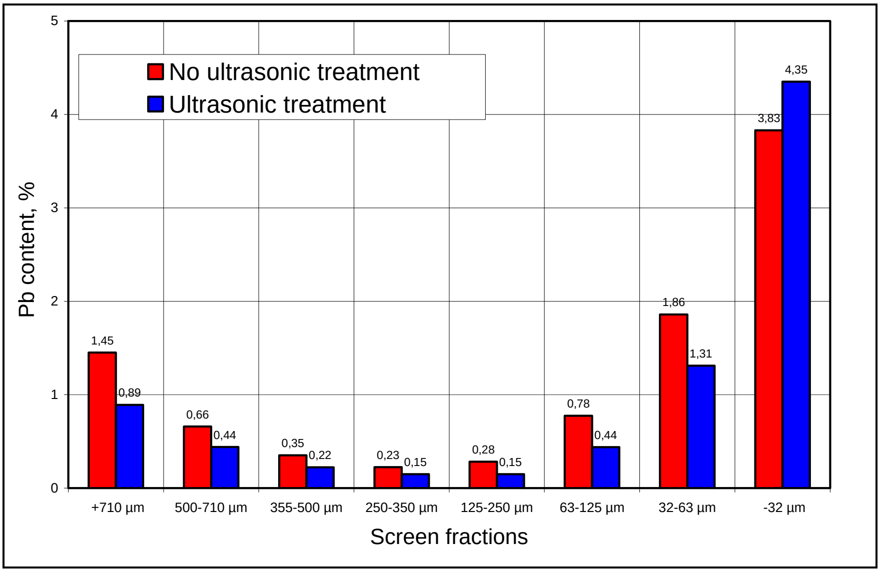


Figure 23. Change in lead content in material fractions as a result of ultrasound treatment.

8.3.2 Ultrasonically assisted flotation tests

When turnip fatty acid was used as the collector chemical in the flotation tests (Fig. 24, experiments 1–4, Table 4), the lead content decreased in the remediated soil from 0.79% to 0.76% (refuse ore in enrichment process) with 15 minutes of ultrasonic treatment. At five minutes of ultrasonic treatment, the lead content decreased to 0.69% (Fig. 24, experiment 3). If the ultrasonic treatment was too long (60 min), the lead content increased slightly. When a sulfide collector was used in the flotation tests, (experiments 7–9), the residual content of heavy metals was much higher. However, ultrasound treatment decreased the metal content slightly also in these experiments. Experiments 13–26 (Fig. 25) were carried out using lower ultrasonic power, shorter treatment time, and treatment pulsation. In these experiments, the effect of ultrasound was not very significant. The ultrasonic treatments were perhaps too weak compared to those in the earlier experiments (Fig. 24), where the original metal concentration was also much higher. Xanthate flotation together with a $CuSO_4$ activator gave the weakest results. Xanthate flotation after sulfide treatment gave the best results. Only marginal fluctuations were obtained in the fatty acid flotation experiments. Thus, further research is needed to see how metal compounds and rock material are bound together, how US effects this binding mechanism and to find out the right flotation conditions.

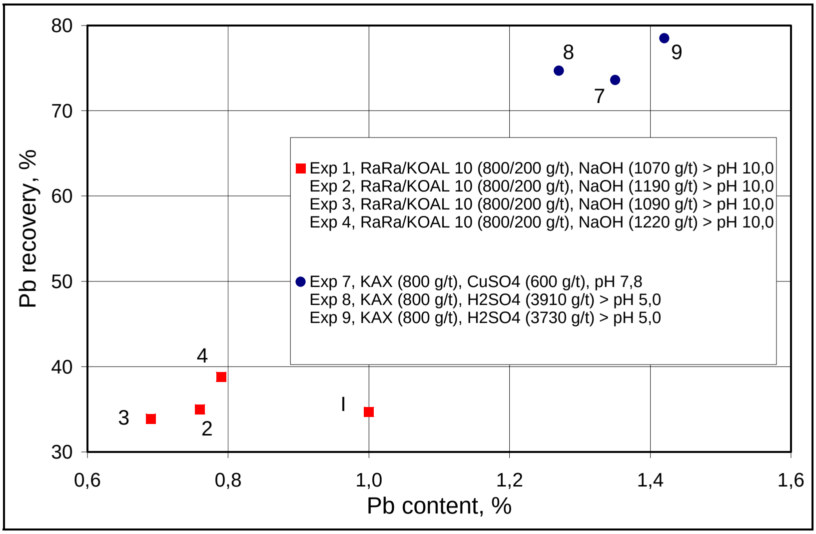


Figure 24. Results of the flotation experiments for the fine soil fractions (< 250 µm) (cleaned soil) at higher ultrasonic power. Experiments 4 and 9 are reference cases without US treatment.

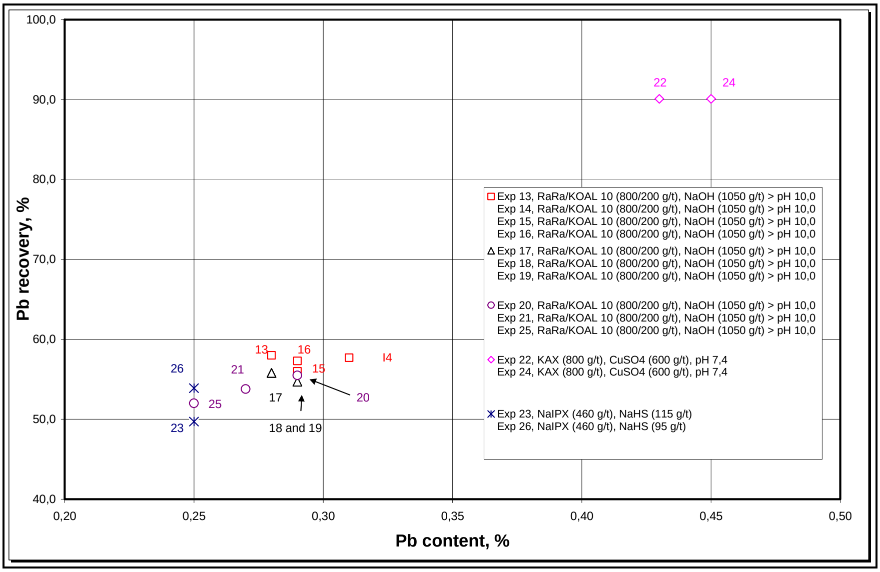


Figure 25. Results of the flotation experiments for the fine soil fractions (< 250 µm) (cleaned soil) at lower ultrasonic power. Experiments 21, 24, and 26 are reference cases without US treatment.

9. Conclusions

In this thesis it was shown that it is possible to use ultrasound on a semi-pilot scale to enhance the disintegration of three quite different samples: polymers, sludge, and contaminated soil.

The results show that PVA degradation occurs when the cavitation threshold is exceeded. When using an ultrasonic input power above the cavitation threshold, the highest intensity value at 20 kHz, according to hydrophone measurements, was 9.5 W/cm^2 and at 40 kHz, 11.4 W/cm^2. Nevertheless, the most extensive degradation of PVA took place at an ultrasonic frequency of 20 kHz. Certainly the higher the applied frequency the shorter the period for cavitation bubbles to grow and collapse, and the smaller the amount of time available to produce cavitation. For this reason, one possible explanation for the degradation was the shear forces created by ultrasonic waves. As the frequency, and hence attenuation, of the wave decreased, the shear forces were complemented by the increased cavitational effects.

Several authors have investigated the effect of solute concentration on degradation. In each case, the extent of degradation has been found to decrease with an increase in solute concentration. Such observations have been interpreted in terms of the increase in viscosity of the solution, *i.e.* the higher the viscosity, the more difficult it becomes to cavitate the solution at a given intensity and the smaller the degradation effect is. In this thesis, the biggest change in RMM was also observed when the concentration of PVA was the lowest, *i.e.* 1% (w/w). But in the case of CMC it was observed that, when viscosity was not adjusted, CMC has an optimal polymer concentration where degradation is the most efficient. The thesis showed that the extent of ultrasonic depolymerization decreases with decreasing molecular mass of the CMC polymer. The study also showed that ultrasonic irradiation causes a narrowing of the molecular mass distribution. The degradation of CMC polymer proceeded linearly and the rate of ultrasonic depolymerization decreased with decreasing molecular mass.

In cases where the initial dynamic viscosities of the polymer solutions were not at the same level, the sonolytic degradation of CMC polymer mainly depended on the initial dynamic viscosity. The higher the initial dynamic viscosity, the faster degradation took place. This was in agreement with ultrasound theory, because the effects resulting from cavitation collapse in viscous liquids were found to be stronger than those caused by collapse in less viscous liquid. The study also showed that when PEG is used to adjust the initial dynamic viscosities, the higher the molecular mass of CMC polymer the faster degradation took place. This was also in agreement with earlier studies, where it has been found that the larger the molecule the faster the degradation. The CMC concentration studies indicated that the higher the polymer concentration the higher the degradation when the initial dynamic viscosity was adjusted using PEG. This was in disagreement with earlier studies where degradation decreased with an increase in solution concentration. However, in those earlier studies the viscosity was not adjusted, which according to this study is one of the main parameters in polymer degradation.

This thesis confirmed the general assumption that the shear forces generated by the rapid motion of the solvent following cavitational collapse are responsible for the breakage of the chemical bonds within the polymer. The effect of polymer concentration could be interpreted in terms of the increase in viscosity with concentration, causing the molecules to become less mobile in solution and the velocity gradients around therefore the collapsing bubbles to become smaller.

This thesis also suggested that ultrasonic disintegration of sludge increases the amount of SCOD and methane production. The multivariate data analysis showed that ultrasonic power, sludge DS, sludge temperature, and ultrasonic treatment time significantly affect sludge disintegration. It was also observed that high ultrasound power together with a short treatment time is more efficient than low ultrasound power with a long treatment time. The effects of ultrasound treatment (20 kHz, 200 W/L) on the methane production of the filtrated fraction of excess sludge were studied in methane production assays using an untreated sample as a control. The longer the treatment time the higher the initial SCOD was in the beginning of the assays. With all the samples, methane production started without any delay. During the 19 days of assays, methane production was 8–17 times higher for the treated samples than for the untreated samples. Methane production per kilogram of SCOD in the sample was the same for samples treated for 2.5 and 10 min, suggesting that the SCOD in these samples was equally degradable despite differences in the quantities of it. Anaerobic batch studies were also performed with 20 differently treated samples of excess sludge. The ultrasound powers ranged up to 300 W/L and the treatment times up to 30 min, while sludge TS ranged from 0.6% to 2.5%. The sludge used in the experiments was obtained from the plant using four different sampling times. In most assays 10–20% more methane was obtained from treated sludge compared to untreated sludge. In general, the higher the SCOD after the treatment the more methane was produced. These results suggest that ultrasound treatment must be optimized separately in each application. When using oxidising agents together with ultrasonic disintegration there was no increase in SCOD and only a slight increase in TOC compared to ultrasonic treatment alone. However, when using oxidizing agents together with ultrasound, no enhancement in methane production was observed. Ultrasound propagation is an important factor in ultrasonic reactor scale-up. Ultrasound efficiency in sludge rose linearly when the input power was close to the transducer. By contrast, ultrasound efficiency even started to decrease when the input power was further away from the transducer.

In this thesis power ultrasound was used as an aiding method for the mineral processing technique, which has recently been developed for the remediation of soil contaminated by heavy metal containing bullets, broken parts thereof, and alteration products. Power ultrasound was used to disperse the soil to remove metals and metal compounds from the soil particle surfaces instead of attrition conditioning. The soil examined came from a former military shooting range. The coarsest material (> 20 mm), which did not contain bullets or parts thereof, was screened out before the ultrasonic treatment experiments. The other screen fractions – 20 mm ↔ 4 mm, 4 mm ↔ 1 mm, < 1 mm, and < 250 μm containing heavy metals – were treated separately in a remediation process, now using ultrasound treatment before separation.

In heavy medium separation, ultrasonic pre-treatment decreased the lead content of the float product of the 4 mm ↔ 1 mm fraction (rock material) from 0.47% to at least 0.15%. Lead recovery from the same product decreased correspondingly from 0.75% to at least 0.3%. In the 20 mm ↔ 4 mm fraction the lead content decreased from 0.17% to at least 0.06%. The decrease in copper content was smaller in the remediated soil. The ultrasonic treatment of the fine test material (< 1 mm) caused a transition in the lead content of the screen fractions. Treatment lowered the lead content in all the fractions except the finest (< 32 μm) fraction. Copper content exhibited a trend similar to the lead content.

The reason for this could be the accumulation of separated Pb and Cu in the finest fraction and ineffective US cleaning with this fraction.

In heavy medium separation, ultrasound improved the remediation results of both products (sink and float products). This was due to the fact that the amount of ultrafine metal fraction was diminished when attrition conditioning was replaced by ultrasound. The remediation process produced float product (cleaned soil) that could be left to its original place. This would reduce process costs and avoid the need to transport large amounts of soil material.

When fatty acid was used as the collector chemical in the flotation tests, the lead content decreased in the remediated soil from 0.79% to 0.76% (refuse ore in enrichment process) with fifteen minutes of ultrasonic treatment. With five minutes of ultrasonic treatment, the lead content decreased to 0.69%. If the ultrasonic treatment was too long (60 min), the lead content increased slightly. When sulfide collector was used in the flotation tests, the residual heavy metal content was much higher. However, ultrasound treatment decreased the metal content slightly also in these experiments. Xanthate flotation together with a $CuSO_4$ activator gave the weakest results. Xanthate flotation after sulfide treatment gave the best results. Only marginal fluctuations were obtained in the fatty acid flotation experiments. Thu, further research is needed to see how metal compounds and rock material are bound together, how US effects this binding mechanism and to determine the right flotation conditions.

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Article I

Ultrasonic depolymerization of aqueous polyvinyl alcohol

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Ultrasonic depolymerization of aqueous polyvinyl alcohol

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Abstract

Ultrasonication has proved to be a highly advantageous method for depolymerizing macromolecules because it reduces their molecular weight simply by splitting the most susceptible chemical bond without causing any changes in the chemical nature of the polymer. Most of the effects involved in controlling molecular weight can be attributed to the large shear gradients and shock waves generated around collapsing cavitation bubbles. In general, for any polymer degradation process to become acceptable to industry, it is necessary to be able to specify the sonication conditions which lead to a particular relative molar mass distribution. This necessitates the identification of the appropriate irradiation power, temperature, concentration and irradiation time. According to the results of this study the reactors constructed worked well in depolymerization and it was possible to degrade aqueous polyvinyl alcohol (PVA) polymer with ultrasound. The most extensive degradation took place at the lowest frequency used in this study, i.e. 23 kHz, when the input power was above the cavitation threshold and at the lowest test concentration of PVA, i.e. 1% (w/w). Thus this study confirms the general assumption that the shear forces generated by the rapid motion of the solvent following cavitational collapse are responsible for the breakage of the chemical bonds within the polymer. The effect of polymer concentration can be interpreted in terms of the increase in viscosity with concentration, causing the molecules to become less mobile in solution and the velocity gradients around the collapsing bubbles to therefore become smaller.

Keywords: Power ultrasound reactors; Depolymerization; PVA

1. Introduction

Most chemists regard sonochemistry as a relatively new branch of chemistry. However, applications of power ultrasound in polymer science date back to the 1930s when sonication of some natural polymers was discovered to reduce viscosity [1]. Schmidt and Rommel first observed the permanent reduction in the viscosity of a polymer solution and attributed it to the breakage of covalent bonds in the polymer chain. They also found that the initial depolymerization rate slowed and stopped completely when the minimum molecular mass was approached. The existence of this limiting degree of polymerization constitutes the basis of most degradation mechanisms [2].

Ultrasonication has subsequently proved to be a highly advantageous method for depolymerizing macromolecules because it reduces their molecular weight simply by splitting the most susceptible chemical bond without causing any changes in the chemical nature of the polymer. It is now well established that prolonged exposure of solutions of macromolecules to high-energy ultrasonic waves produces a permanent reduction in viscosity. Even when the irradiated polymers are isolated and redissolved their viscosity remains low in comparison with that of non-irradiated solutions [3].

Most effects in sonochemistry arise from cavitation. While some consequences of this, such as radical production, are used in the manufacture of polymers, the exact origin of the effects, whether from thermal ‘hot spots’ or electrical or coronal discharges, is relatively unimportant to the polymer chemist. Most of the effects involved in controlling molecular weight can be attributed to the large shear gradients and shock waves generated around collapsing cavitation bubbles [1].

Earlier studies have shown that the degradation is caused by

1. the hydrodynamic forces of cavitation, i.e. the shock wave energy released on bubble implosion;
2. the shear stresses at the interface of the pulsating bubbles;
3. the associated thermal and pressure increases within the bubbles themselves [2].

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In general, for any polymer degradation process to become acceptable to industry, it is important to be able to specify the sonication conditions which lead to a particular relative molar mass (RMM) distribution. This necessitates the identification of the appropriate irradiation power, temperature, concentration and irradiation time [4].

The aim of the present work was to study the effect of ultrasonic input power and ultrasonic frequency at three aqueous solution concentrations on the degradation of polyvinyl alcohol (PVA) with ultrasonic reactors constructed in this study (Fig. 1).

2. Experimental

2.1. Reactors

Three ultrasonic reactors operating at 23, 40 and 900 kHz were constructed in this study. The volume of reactors was 10 l. The 23 and 40 kHz round-shaped reactors were made of steel. The rectangular-shaped 900 kHz reactor was made of plastic. The 23 kHz reactor had five and the 40 kHz reactor seven Langevin-type transducers installed on the bottom of the reactors. The surface of the 900 kHz transducer formed the entire bottom of the rectangular-shaped reactor.

2.2. Hydrophone measurements

There are many types of acoustic probe that can be used to measure the pressure amplitude in the system. In principle, the local acoustic power can be obtained by measuring the pressure amplitude P, the velocity v of an imaginary particle submitted to the field, and their phase difference $\mathbf{Y}$. Transmitted power can then be obtained by integrating $Pv\cos\mathbf{Y}$ over the total volume. This is a good method for local measurements, but rather tedious for overall power. Furthermore, particle velocity has to be measured in order to calculate the ultrasonic power and this is not a trivial task. Indeed, particle velocity may be assumed to be the same in the liquid and at the tip of the probe. Although this is almost never exactly true, this assumption can lead to a reasonable estimate of the dissipated ultrasonic power. Acoustic probes are widely used to calibrate ultrasonic equipment [5].

Fig. 1. Ultrasonic reactors constructed in this study.

In this study the calibration of the reactors constructed in this study were done by using hydrophone measurements. On the other hand, the hydrophone measurements show the intensity of ultrasonic power. It is important to know the intensity of ultrasonic power when considering how much power is needed to depolymerization.

Acoustic impedance (z) is the relation ship between sound power (p) and particle velocity (v). The acoustic impedance to a planewave is

$$z = \frac{p}{v} = \rho c \tag{1}$$

where ρ is the density of the medium and c is the velocity of sound in the medium.

One measure of the sound wave's power magnitude is the acoustic intensity of sound. The acoustic intensity indicates the sound power which hits a particular surface (W/m^2). Acoustic intensity has only a limited practical meaning because it is impossible to measure its magnitude directly. Nevertheless acoustic intensity is a very useful magnitude when determining ultrasonic power. In the case of vertical sonication of a surface, acoustic intensity is determined by Eq. (2):

$$I = \frac{p^2}{z} \tag{2}$$

where p is the power of the sound and z the acoustic impedance of the medium.

The effective value of voltage is often defined by

$$\begin{aligned} &U_{\mathrm{eff}} = \sqrt{2}/2U_0 \\ &\text{so} \quad U_{\mathrm{eff}} = U_0/\sqrt{2} \end{aligned} \tag{3}$$

A hydrophone measures the power of sound as the voltage from peak to peak. Thus the hydrophone value of the voltage has to be divided by 2 and so the effective value of the voltage is

$$U_{\mathrm{eff}} = \frac{U_{\mathrm{hydrophone}}}{2\sqrt{2}} \tag{4}$$

A voltage efficiency of the hydrophone is a value which depends on hydrophone. It must be noted in sound power measurement. The voltage efficiency of the hydrophone is mentioned in the calibration papers of each hydrophone. Knowing the effective voltage and the voltage efficiency of the hydrophone it is possible to calculate the power of sound which meets the hydrophone's square surface area:

$$p = \frac{U_{\text{eff}}}{\text{voltage efficiency of the hydrophone}} \qquad (5)$$

By measuring the power of sound using a hydrophone at different places within a reactor and using Eqs. (1)–(4), it is possible to calculate the acoustic intensity of ultrasound [6].

2.3. Depolymerization methods

PVA obtained from BDH laboratory supplies (average molecular mass 115 000) was used to prepare PVA solutions at three concentrations (1%, 2% and 3% (w/w)) having a mass of 5000 g. No purification of the commercial PVA was carried out and the ultrasonic treatments were performed at room temperature. Initially, the effect of ultrasonic input power on depolymerization was studied, and after that the depolymerization experiments were performed at two different ultrasonic input powers one below and another above the cavitation threshold. It is quite difficult to measure cavitation threshold but it is known that in water when the ultrasonic frequency is 20 kHz the threshold is about 0.4–4.0 W/cm^2 (depends on air content of water). Measured viscosities of PVA were only a little bit higher than the viscosity of water and thus the cavitation threshold of PVA should be quite equal to water [3]. The hydrophone measurements showed that by using ultrasonic input power of 10 W the ultrasonic intensities in the middle of reactor were 0.0–3.2 W/cm^2 and by using input power of 200 W the ultrasonic intensities were 6.4–11.4 W/cm^2. So the input power below cavitation threshold used at 23 and 40 kHz were 10 W and above cavitation threshold 200 W. At 900 kHz powers used were 120 and 600 W. The input power of 23 and 40 kHz reactors was adjusted using an ENI Model 1104LA amplifier and frequencies were set using an Electronics function generator 8553. The power of the 900 kHz reactor was adjusted using a HI Megasonic 600 KAIJO. Each solution was irradiated for 2 h and samples were withdrawn for analysis at 30, 60, 90 and 120 min. The dynamic viscosity of PVA solutions before and after sonication was measured using a Haake VT 501 viscometer at room temperature.

3. Results

3.1. Hydrophone measurements

Initially the effect of ultrasonic input power on ultrasonic intensity was studied from hydrophone measurements. Results showed the potential for measuring ultrasonic intensity by this method. Ultrasonic intensity increased linearly when the ultrasonic input power increased up to 500 W (Fig. 2).

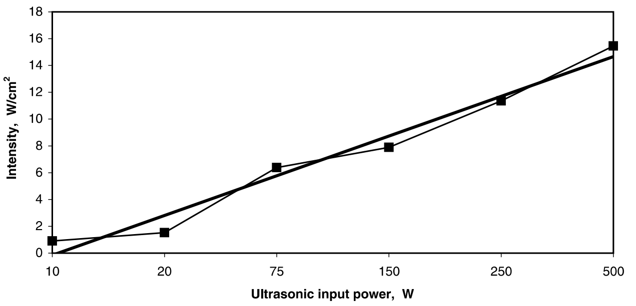

Fig. 2. The intensity of ultrasound in water as a function of ultrasonic input power. The measurement point was at the centre of the reactor 6 cm from the bottom. The reactor operated at 23 kHz.

The hydrophone measurements revealed several hot spots in the reactors, where ultrasonic intensity was greater than in the surrounding areas (Fig. 3). The hydrophone measurements therefore verified that ultrasound is a wave motion with alternating power maxima and minima.

The hydrophone measurements also showed that there were no dead spots in the reactors and that the ultrasonic intensity was up to 15.5 W/cm^2. The hydrophone measurements from the 23 kHz reactor in 5 l water are presented in Fig. 4. The measured layer was 6 cm from the bottom of the reactor and the ultrasonic input power was 200 W.

3.2. The effect of ultrasonic input power

Depolymerization studies showed that viscosity decreased further when the ultrasonic input power was increased. The input powers tested were 10, 50, 100, 200 and 350 W. Up to 100 W, the decrease in viscosity seems to be greater than in the range from 100 to 350 W (Fig. 5). At 23 and 40 kHz the input powers below (10 W) and

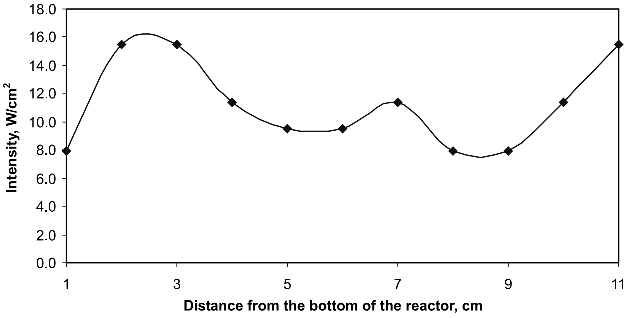

Fig. 3. Hydrophone measurements at the centre of the 23 kHz reactor. Ultrasonic input power was 500 W.

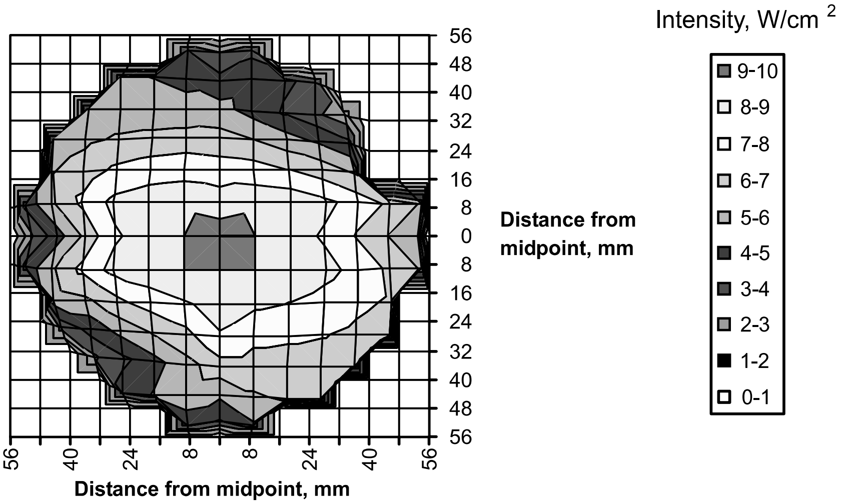

Fig. 4. Hydrophone measurements from the reactor operating at 23 kHz. The ultrasonic input power was 200 W, the volume of water was 5 l and the hydrophone was 6 cm from the bottom of the reactor.

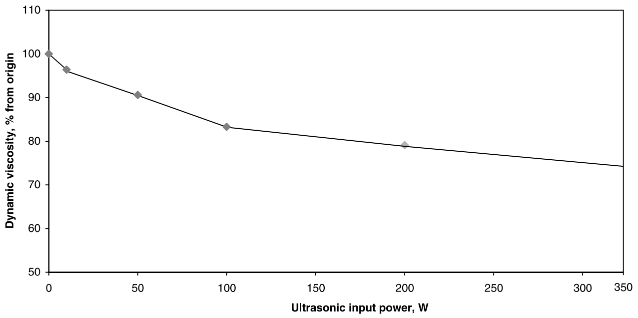

Fig. 5. The change in dynamic viscosity as a function of ultrasonic input power using 2% PVA and a 23 kHz ultrasonic transducer.

above (200 W) the cavitation threshold were used, while input powers of 120 and 600 W were used at 900 kHz.

Examination of the effect of ultrasonic input power showed that depolymerization of PVA requires the power to exceed the cavitation threshold. At an input power below the cavitation threshold there was only a slight decrease in viscosity. Even in the best situation, when the hydrophone measurements indicated a slight cavitation in the hot points of the 23 and 40 kHz reactors, the decrease in viscosity was only about 10% (Table 1).

Table 1
Changes in the dynamic viscosity of PVA after 2 h ultrasonication at different concentrations when the ultrasonic input power was below the cavitation threshold

PVA concentration (w/w)	Dynamic viscosity, percentage of the initial value		
	23 kHz, 10 W	40 kHz, 10 W	900 kHz, 120 W
1%	90	90	96
2%	91	96	98
3%	90	94	97

When the ultrasonic input power was above cavitation threshold the decrease in viscosity was at least 14% and in the best situation 31% below the initial value (Table 2).

3.3. The effect of ultrasonic frequency

At an ultrasonic input power above the cavitation threshold depolymerization was greater at low (23 kHz) than at high (900 kHz) frequency (Table 2). The viscosity at 23 kHz decreased in the best situation to 31% below the initial value. By contrast, the decrease at 900 kHz, even in the best situation, was only to 4% below the initial value (Table 3).

3.4. Relative molar mass of PVA after sonication

The RMM of PVA before and after ultrasonic treatment was measured using two different methods. At first, an attempt was made to measure RMM by gel permeation chromatographic analysis. The absorption peak of the solvent dimethylsulfoxide (DMSO) was unfortunately in the same area as the absorption peak of

Table 2
Changes in the dynamic viscosity of PVA after 2 h ultrasonication at different concentrations when the ultrasonic input power was above the cavitation threshold

PVA concentration (w/w)	Dynamic viscosity, percentage of the initial value		
	23 kHz, 200 W	40 kHz, 200 W	900 kHz, 600 W
1%	85	84	77
2%	71	75	86
3%	69	80	86

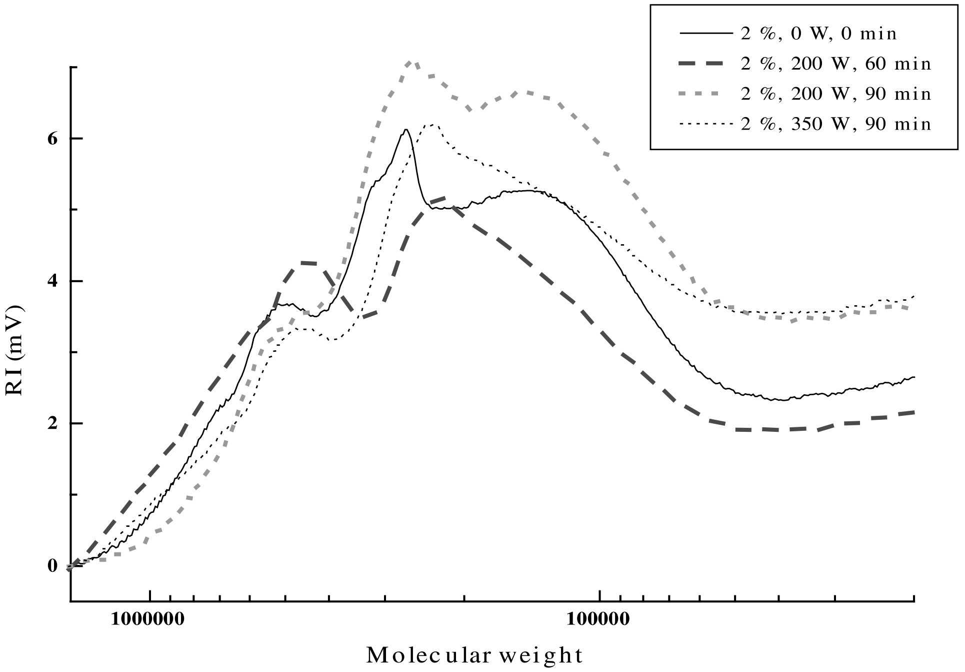

Fig. 6. Measurement of relative molar mass by gel permeation chromatographic analysis.

PVA making it difficult to measure the RMM of the polymer (Fig. 6).

The second method to measure the RMM was viscosity calibration. The viscosity of three commercial PVA polymers with RMMs of 22 000, 72 000 and 115 000 was measured and used to draw a calibration curve. Viscosity calibration showed that the RMM of PVA with a concentration 1% (w/w) was about 30 000 after sonication. In the case of PVA at concentrations of 2% and 3% (w/w) the RMMs were about 60 000 and 75 000 after sonication. The calibration curve of the 2% (w/w) solution is shown in Fig. 7.

The viscosity calibration showed that although the biggest changes in dynamic viscosity were in the 3% (w/w) polymer solution (Table 3), the greatest decrease in relative molar mass occurred with the PVA concentration of 1% (w/w).

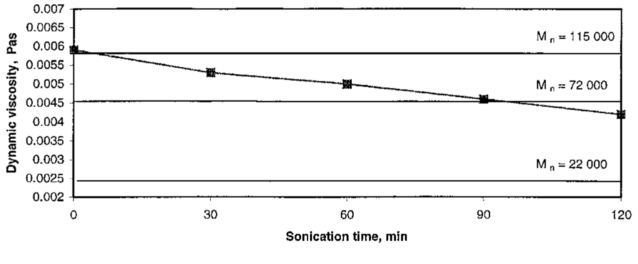

Fig. 7. The viscosity calibration of 2% (w/w) PVA solution. The ultrasonic input power was 200 W and the frequency 23 kHz.

Table 3
Changes in the dynamic viscosity of PVA after 2 h ultrasonication at different concentrations subject to different ultrasonic frequencies with an ultrasonic input power of about 200 W

PVA concentration (w/w)	Dynamic viscosity, percentage of the initial value		
	23 kHz, 200 W	40 kHz, 200 W	900 kHz, 120 W
1%	85	84	96
2%	71	75	98
3%	69	80	97

4. Conclusions

The reactors constructed in this study worked well in depolymerization and it was possible to degrade PVA polymer with ultrasound.

In earlier publications it has been reported that the higher the frequency of the ultrasonic wave, the more rapidly it is attenuated. However, it is important to recognize that when comparing the effects of frequency, intensity must be held constant [3]. In this study, when using an ultrasonic input power of 200 W, the highest intensity value at 23 kHz according to hydrophone measurements was 9.5 W/cm^2 and at 40 kHz, 11.4 W/cm^2. Nevertheless, the most extensive degradation took place at an ultrasonic frequency of 23 kHz. Certainly the higher the applied frequency the shorter the period for cavitation bubbles to grow and collapse, and the smaller the amount of time available to produce cavitation. Thus one possible explanation for the degradation is the shear forces created by ultrasonic waves. As the frequency, and hence attenuation, of the wave decreases, the shear forces will be complemented by the increased cavitational effects [3].

Mason and Lorimer have posited the existence of cavitation threshold, i.e. a limit of sound intensity below which cavitation could not be produced in a liquid. They suggested that only when the applied acoustic amplitude of the ultrasonic wave was sufficiently large to overcome the cohesion forces within the liquid could the liquid be torn apart to produce cavitation bubbles. If degradation is due to cavitation then it is to be expected that degradation will only occur when the cavitation threshold is exceeded. This is confirmed, e.g., by Weissler, who investigated the degradation of hydroxycellulose and observed that the start of degradation coincided with the onset of cavitation [3]. The degradation of PVA in this study was also only observed when the input power was above cavitation threshold. It is quite difficult to measure cavitation threshold but it is known that in water when the ultrasonic frequency is 20 kHz the threshold is about 0.4–4.0 W/cm^2 (depends on air content of water). Measured viscosities of PVA were only a little bit higher than the viscosity of water and thus the cavitation threshold of PVA should be quite equal to water [3]. According to this study the degradation of PVA will therefore occur when the cavitation threshold is exceeded.

Several authors have investigated the effect of solute concentration on degradation. In each case the extent of degradation has been found to decrease with an increase in solute concentration. Such observations have been interpreted in terms of the increase in viscosity of the solution, i.e. the higher the viscosity, the more difficult it becomes to cavitate the solution at a given intensity and the smaller is the degradation effect [3]. In this study the biggest change in RMM was also observed when the concentration of PVA was the lowest, i.e. 1% (w/w).

This study confirms the general assumption that the shear forces generated by the rapid motion of the solvent following cavitational collapse are responsible for the breakage of the chemical bonds within the polymer. The effect of polymer concentration can be interpreted in terms of the increase in viscosity with concentration, causing the molecules to become less mobile in solution and the velocity gradients around the collapsing bubbles to therefore become smaller [1].

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Article II

Ultrasonic depolymerization of aqueous carboxymethylcellulose

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Ultrasonic depolymerization of aqueous carboxymethylcellulose ☆

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Abstract

Prolonged exposure of solutions of macromolecules to high-energy ultrasonic waves produces a permanent reduction in viscosity. However, the exact mechanism by which degradation occurs is still open to discussion. According to this study hydrodynamic forces played the primary role in degradation process. This study showed that there is an optimal carboxymethylcellulose (CMC) concentration to the most efficient degradation. Ultrasound degraded preferentially large CMC molecules and cleavage took place roughly at the centre of the CMC molecules. Degradation of CMC did not proceed below a certain molecular mass. During ultrasonic degradation the molecular mass distribution narrowed. For any polymer degradation process to become acceptable to industry, it is important to be able to specify the sonication conditions to produce a particular relative molecular mass distribution.

Keywords: Ultrasonic depolymerization; Carboxymethylcellulose; Power ultrasound; Degradation; Polymer concentration; Relative molecular mass

1. Introduction

It is well established that prolonged exposure of solutions of macromolecules to high-energy ultrasonic waves produces a permanent reduction in viscosity. Even when the irradiated polymers are isolated and redissolved their viscosity remains low in comparison with the non-irradiated solutions [1].

The exact mechanism by which degradation occurs is still open to discussion. It is generally agreed that the hydrodynamic forces have the primary importance. Hydrodynamic forces may originate as a result of increased frictional forces between the ultrasonically accelerated faster moving solvent molecules and the larger, less mobile, macromolecules. Hydrodynamic forces may also be due to the high pressure associated with the collapse of cavitation bubbles [2,3].

It is believed, that ultrasonic degradation, unlike chemical or thermal decomposition, is a non-random process, with cleavage taking place roughly at the centre of the molecule and with larger molecules degrading the fastest. It is also known, that there is a certain molecular weight below which degradation does not take place. Price et al. claims that this limiting molecular weight has the added effect of narrowing the molecular weight distribution [2]. In earlier studies it has been noticed that the rate of ultrasonic depolymerization decreases with decreasing molecular weight of the polymer, and that the initial structure of the molecule, rather than its size, determines whether it will be broken by this means. The rate and the extent of degradation depends on the duration of irradiation, concentration of solution, nature of polymer and solvent, and the intensity of the ultrasound, in accord with the effect of experimental parameters on cavitation [2,4,5]. Several authors have investigated for example the effect of solution concentration on degradation and in every case the rate and the extent of degradation have been found to decrease with an increase in concentration [1]. However, cavitation is difficult to achieve in viscous materials corresponding to high-molecular-weight polymers. For this reason, dilute solutions of the polymers have been used for the study of ultrasonic depolymerization [6].

Several authors have investigated the effect of solute concentration on degradation. In each case the extent of degradation has been found to decrease with an increase

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in solute concentration. Such observations have been interpreted in terms of the increase in viscosity of the solution. It is known that the formation of cavitation in the liquid requires that the negative pressure in the rarefraction region of wave function must overcome the natural cohesion forces acting within the liquid. Therefore cavitation should be more difficult to produce in viscous liquids, where the forces are stronger and waves with greater amplitude and hence greater intensity will be necessary. Thus, the higher the viscosity the more difficult it becomes to cavitate the solution at a given intensity and the smaller is the degradation effect. On the contrary, the effects resulting from cavitation collapse in viscous liquids are stronger than collapse in less viscous liquid [1].

In general, for any polymer degradation process to become acceptable to industry, it is important to be able to specify the sonication conditions, which lead to a particular relative molar mass (RMM) distribution. This necessitates the identification of the appropriate irradiation power, temperature, concentration and irradiation time [7,8].

The aim of the present work was to study the effect of polymer concentration and molecular mass distribution on the degradation of carboxymethylcellulose (CMC) polymers.

2. Experimental

2.1. Reactor

Ultrasonic reactor operating at the frequency of 23 kHz was used in depolymerization. The volume of this round-shaped stainless steel reactor was 10 l. Five Langevin-type transducers were installed on the bottom of the reactor. The characteristics and the optimal operating range of the reactor used are detailed in earlier study [9].

2.2. Depolymerization methods

Nine carboxymethylcellulose (CMC 1–CMC 9) samples obtained from Noviant Oy had initial RMM from 14,000 to 335,000 (see Table 1).

Table 1
The initial relative molecular mass of the CMC samples

Sample	RMM (g/mol)
CMC 1	14,000
CMC 2	20,000
CMC 3	28,000
CMC 4	32,000
CMC 5	127,000
CMC 6	150,000
CMC 7	226,000
CMC 8	296,000
CMC 9	335,000

No purification of the commercial CMC samples was carried out. The ultrasonic input power of 200 W at 23 kHz was adjusted using an ENI Model 1104LA amplifier. Frequency was set using an Electronics function generator 8553. The temperature of the ultrasonic reactor was adjusted to +40 ± 2 °C during sonication. Each solution was irradiated for 3 h and samples were withdrawn for analysis at 30, 60, 90, 120, 150, and 180 min. The dynamic viscosity of the CMC solutions before and after sonication was measured at room temperature using a Haake VT 501 viscometer. The RMM measurements were obtained using Waters 501 HPLC with Waters 717 autosampler, Jordi Gel GBR 500A column and Polymer Laboratories PL-ELS 1000 detector.

3. Results and discussion

3.1. Reproducibility of ultrasonic degradation

The reproducibility of ultrasonic degradation and the stability of the viscosity reduction were studied using CMC 5 and CMC 9 polymers. Ultrasonic irradiation produced a permanent reduction in viscosity. The viscosity was measured one month after ultrasonic treatment. The viscosity values were within 3% of the previous values measured immediately after the cessation of irradiation. The ultrasonic degradation was also reproducible. The viscosity of the polymers studied decreased equally in both cases (Fig. 1). It was also seen that the viscosity decreased principally during the first three hours of ultrasonic treatment.

3.2. Effect of the CMC concentration

The effect of polymer concentration on degradation was studied using CMC 5 polymer. Aqueous solutions with concentrations of 0.5%, 1.0%, 1.5%, 2.0%, 3.0% w/w were used in the experiments. The total mass of the solutions were 2500 g. The concentration studies showed that there is an optimal CMC concentration for the most efficient degradation. The optimum polymer con-

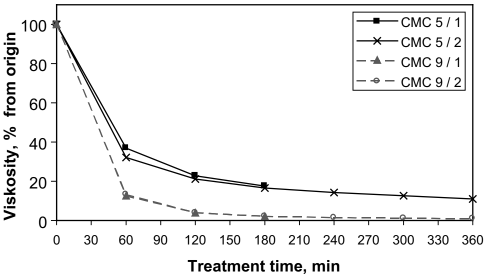

Fig. 1. Reproducibility of ultrasonic degradation of CMC 5 and CMC 9.

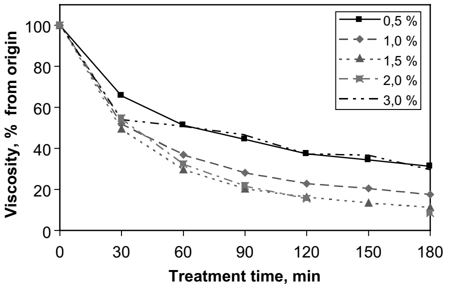

Fig. 2. The effect of polymer concentration on degradation of CMC 5.

centration for degradation of CMC 5 was 1.5–2.0% w/w (Fig. 2).

The effect of solution concentration on degradation has been investigated earlier by several authors. In every case the extent of degradation have been found to decrease with increase in concentration. This is in disagreement with the results achieved in this study where the most efficient degradation was achieved in optimal polymer concentration. Viscosity is dependent on the concentration of polymer. When the concentration is smaller than the optimal concentration the shear forces due to low viscosity are not strong enough to cause efficient degradation. When the concentration is higher than the optimal concentration the polymer molecules become less mobile in solution due to high viscosity and the velocity gradients around the collapsing bubbles become smaller. Thus, this study confirmed the general assumption that the shear forces generated by the rapid motion of the solvent are responsible for the breakage of the chemical bonds within the polymer.

3.3. Effect of the initial relative molecular mass of polymer

The effect of initial RMM of all the nine CMC polymers on the degradation rate was studied for an initial concentration of 1.0% w/w. The viscosity decreased significantly for those polymers having large RMM (Fig. 3). The viscosity decrease was minor with the polymers having small RMM. Thus, the extent of ultrasonic depolymerization decreased with decreasing molecular mass of the polymer. The studies showed also that the degradation of molecules continued only to a certain limiting molecular mass. This is in agreement with the results obtained in earlier studies [2]. The molecular mass limit of the CMC polymer was about 0.0040 Pas. Below the limit, the polymer chain was so short that it followed ultrasonic vibration flexibly and cleavage at the centre of the molecule did not take place anymore.

The RMM studies above were undertaken using 1.0% w/w CMC 1–CMC 9 samples which had different initial viscosities. According to the literature [1], viscosity has an influence on degradation. Hence the result of RMM studies had to be verified using polymers with different RMM but the same viscosity. The verification studies gave similar results to those obtained when the samples had different viscosities (Fig. 4). The viscosity decreased more and faster with the polymers having higher RMM.

According to this examination the extent of ultrasonic depolymerization decreased with decreasing molecular mass of the CMC polymer. This observation strengthens the claim that ultrasonic degradation, unlike chemical or thermal decomposition, is a non-random process with cleavage taking place roughly at the centre of the molecule and with larger molecules degrading the fastest.

3.4. Relative molecular mass of CMC after sonication

The RMM of CMC before and after ultrasonic treatment was measured using two different methods; gel permeation chromatographic analysis (HPLC) and viscosity calibration. According to HPLC-examinations, depolymerization had the added effect of narrowing the molecular mass distribution (Fig. 5). The main reason for the narrowing was the limiting molecular mass. Initially the solution contained polymers with different molecular mass. After sonication, the solution contained an increase in polymer with chain lengths which could not be shortened anymore resulting in a narrower molecular mass distribution.

Viscosities were converted to RMM by using a viscosity calibration curve ($M = 70014\ln(\eta) + 345108$). The calibration curve was determined by measuring the viscosities of five commercial CMC polymers with RMMs of 127,000, 150,000, 226,000, 296,000, and 335,000. When

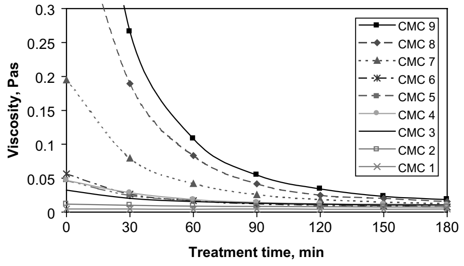

Fig. 3. The viscosity of CMC samples in the function of depolymerization time.

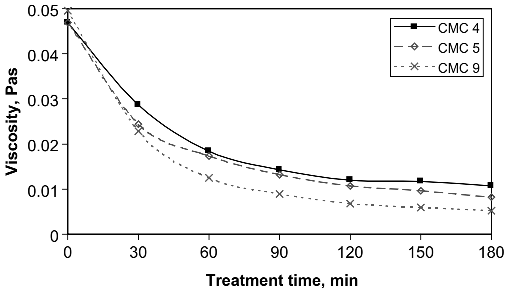

Fig. 4. The depolymerization of CMC samples which have the same viscosity but different relative molecular mass.

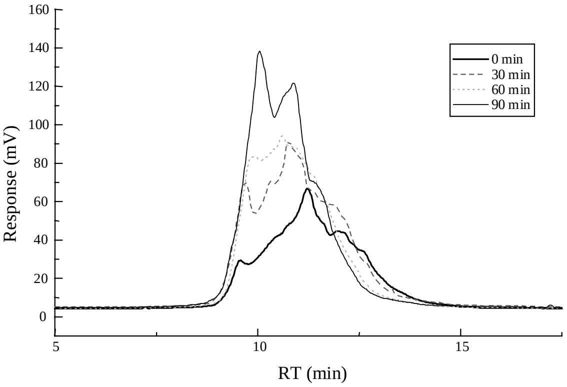

Fig. 5. Measurement of relative molecular mass by the gel permeation chromatographic analysis.

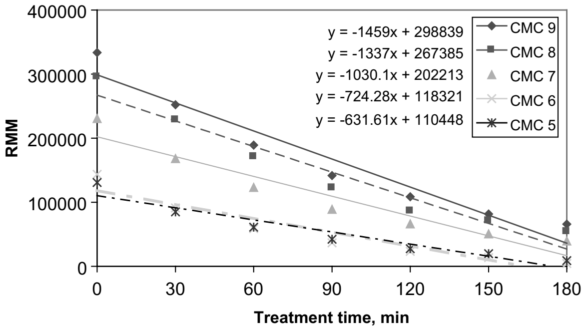

Fig. 6. The relative molecular mass of CMC polymer versus treatment time.

the RMMs were plotted as a function of irradiation time the plot was linear in nature (Fig. 6). It was also observed that the rate of ultrasonic depolymerization decreased with decreasing molecular mass of the polymer.

4. Conclusions

The aim of this research was to study the effect of polymer concentration and molecular mass distribution on the degradation of CMC polymers. The study showed that the aqueous CMC has an optimal polymer concentration where degradation is the most efficient. The extent of ultrasonic depolymerization decreases with decreasing molecular mass of the CMC polymer. The study showed also that the ultrasonic irradiation causes narrowing of the molecular mass distribution. The degradation of CMC polymer proceeds linearly and the rate of ultrasonic depolymerization decreases with decreasing molecular mass.

Acknowledgements

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Article III

Ultrasonic degradation of aqueous carboxymethylcellulose: Effect of viscosity, molecular mass, and concentration

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Ultrasonic degradation of aqueous carboxymethylcellulose: Effect of viscosity, molecular mass, and concentration ☆

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Abstract

It is well established that prolonged exposure of solutions of macromolecules to high-energy ultrasonic waves produces a permanent reduction in viscosity. It is generally agreed as well and also this study proved the hydrodynamic forces to have the primary importance in degradation. According to this study the sonolytic degradation of aqueous carboxymethylcellulose polymer or polymer mixtures is mainly depended on the initial dynamic viscosity of the polymer solution when the dynamic viscosity values are in the area range enabling intense cavitation. The higher was the initial dynamic viscosity the faster was the degradation. When the initial dynamic viscosities of the polymer solutions were similar the sonolytic degradation was dependent on the molecular mass and on the concentration of the polymer. The polymers with high molecular mass or high polymer concentration degraded faster than the polymers having low molecular mass or low polymer concentration. The initial dynamic viscosities were adjusted using polyethyleneglycol.

Keywords: Ultrasound; Degradation; Carboxymethylcellulose; Cavitation; Viscosity; Molecular mass; Concentration; Polyethyleneglycol

1. Introduction

It is well established that prolonged exposure of solutions of macromolecules to high-energy ultrasonic waves produces a permanent reduction in viscosity. Even when the irradiated polymers are isolated and redissolved their viscosity remains low in comparison with the non-irradiated solutions [1, p. 99].

The exact mechanism by which degradation occurs is still open to discussion. It is generally agreed that the hydrodynamic forces have the primary importance. Hydrodynamic forces may originate as a result of increased frictional forces between the ultrasonically accelerated faster moving solvent molecules and the larger, less mobile, macromolecules. Hydrodynamic forces may also be due to the high pressure associated with the collapse of cavitation bubbles [2, p. 156,3,4, p. 151].

It is believed, that ultrasonic degradation, unlike chemical or thermal decomposition, is a non-random process, with cleavage taking place roughly at the centre of the molecule and with larger molecules degrading the fastest. In addition it is known, that below a certain molecular weight degradation does not take place. Price et al. claims that this limiting molecular weight has the added effect of narrowing the molecular weight distribution [3]. In earlier studies it has been noticed that the rate of ultrasonic depolymerization decreases with decreasing molecular mass of the polymer, and that the initial structure of the molecule, rather than its size, determines whether it will be broken by this means. The rate and the extent of degradation depend on the duration of irradiation, nature of polymer and solvent, and the intensity of the ultrasound, in accord with the effect of experimental parameters on cavitation [2, pp. 99–126,4, p. 151,5, pp. 125–129,6, p. 403,7–18].

The effect of concentration on ultrasonic degradation has also been under investigations. It has been found that

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the extent of degradation decreases with an increase in solution concentration or that there is an optimum polymer concentration for degradation [1, pp. 115–117,11,15, 18–20]. In general, the increase of polymer concentration increases the viscosity of the solution, and thus the decrease in degradation has been interpreted in terms of the increased viscosity. It is known that the formation of cavitation in the liquid requires that the negative pressure in the rare fraction region of wave function must overcome the natural cohesion forces acting within the liquid. Therefore cavitation is more difficult to produce in viscous liquids, where the forces are stronger. Thus, waves with greater amplitude and hence greater intensity will be necessary. For this reason, dilute solutions of the polymers have been used for the study of ultrasonic depolymerization [6, p. 403]. On the other hand, the effects resulting from cavitation collapse in viscous liquids are stronger than collapse in less viscous liquid [1, p. 107].

In earlier investigations the effects of molecular mass, concentration and viscosity of polymers have been studied interdependently. However, if the effect of a single parameter has to be clarified, especially the viscosity and the concentration have to be studied separately. The aim of this study was to examine the effect of viscosity, molecular mass and concentration of polymer on ultrasonic degradation independently.

2. Experimental

2.1. Ultrasonic degradation

Ultrasonic degradation experiments were carried out using a round-shaped ultrasonic reactor made of stainless steel. The volume of the reactor was 10 l. Five Langevin-type transducers operating at the frequency of 23 kHz were installed on the bottom of the reactor. The input irradiation power was adjusted using an ENI Model 1104LA amplifier and the frequency was set using an electronics function generator 8553. The characteristics and the optimal operating range of the reactor used are detailed in the earlier study [21].

In general, for any polymer degradation process to become acceptable to industry, it is important to be able to specify the sonication conditions (appropriate irradiation power, irradiation frequency, temperature, concentration and irradiation time), which lead to a particular relative molar mass (RMM) distribution [19,22]. In this study the ultrasonic input power was 80 W/l at 23 kHz, which were found to be the best sonication conditions for the polymer degradation studies in preliminary tests. The temperature was adjusted to +40 ± 2 °C during sonication in order to make the degradation experiments comparable. Every polymer solution was irradiated either 1 or 3 h. Samples in 1 h cases were withdrawn for viscosity analysis at 0, 5, 15, 30, and 60 min and in 3 h cases at 0, 5, 15, 30, 60, 90, 120, 150, and 180 min. The reproducibility of the ultrasonic degradation was determined (see Chapter 3.1).

2.2. Polymers

Nine carboxymethylcellulose (CMC) samples delivered by CP Kelco, Noviant, were used in the study. The initial relative molecular mass (RMM) of the CMC polymers ranged from 14,000 to 335,000 (Table 1).

Experiments were carried out using two types of polymer solutions; solutions with a single polymer or polymer mixtures with two different polymers (Table 2). The effect of the initial dynamic viscosity on the change of dynamic viscosity was studied using all the nine CMC polymers. The effect of the molecular mass on degradation was studied using the CMC 5–9 polymers. The effect of the polymer concentration on degradation was studied using the CMC 5 polymer. No purification of the commercial CMC polymers was carried out. The total mass of the treated aqueous solution was 2500 g. The polymer concentration was 1.0% w/w except in concentration studies when the concentration varied from 0.25% to 3% (see Chapter 2.3).

2.3. Viscosity and concentration

The dynamic viscosity of the CMC solutions before and after sonication was measured at room temperature using a Haake VT 501 viscometer with NT rotor. It was impossible to adjust the initial dynamic viscosities of CMC polymer mixtures to the same level when using different CMC polymers (Table 2). That is because the viscosity of CMC is not directly proportional either to the concentration or molecular mass of CMC. On the other hand, it is not possible to study the effects of the chosen parameters independently without adjusting initial dynamic viscosity using another inert polymer. Thus, polyethyleneglycol (PEG) was chosen for viscosity adjustment. PEG is not affected by ultrasonic irradiation when the temperature is adjusted as can be seen in Chapter 3.3.

In the concentration studies the amount of polymer concentration varied while at the same time the initial dynamic viscosities had to be the same. The initial dynamic viscosity was also in this case adjusted using PEG. The concentration study was carried out at two viscosity levels. The concentrations from 0.25% to 1.00% w/w were adjusted to the initial dynamic viscosity level of ~35 mPas and the concentrations from 1.00% to 3.00% w/w to the initial dynamic viscosity level of ~400 mPas.

Table 1
Initial relative molecular mass (RMM) of the CMC polymers

Polymer	RMM
CMC 1	14,000
CMC 2	20,000
CMC 3	28,000
CMC 4	32,000
CMC 5	127,000
CMC 6	150,000
CMC 7	226,000
CMC 8	296,000
CMC 9	335,000

Table 2
Amount of single CMC polymers and initial dynamic viscosities of the polymer mixtures

Sample	Polymer	Polymer/g	Initial dynamic viscosity/mPas
Mix 1	CMC 6	22.5	26.7
	CMC 1	2.5	
Mix 2	CMC 7	15.0	17.4
	CMC 1	10.0	
Mix 3	CMC 7	16.0	53.6
	CMC 1	8.0	
Mix 4	CMC 8	12.5	40.0
	CMC 1	12.5	
Mix 5	CMC 8	12.5	40.3
	CMC 1	12.5	
Mix 6	CMC 8	12.5	41.3
	CMC 1	12.5	
Mix 7	CMC 8	12.5	40.8
	CMC 1	12.5	
Mix 8	CMC 6	22.0	47.5
	CMC 2	3.0	
Mix 9	CMC 8	11.3	51.5
	CMC 2	13.8	
Mix 10	CMC 6	22.0	43.4
	CMC 3	3.0	
Mix 11	CMC 8	10.5	68.9
	CMC 3	14.5	
Mix 12	CMC 6	23.0	47.5
	CMC 4	2.0	
Mix 13	CMC 8	10.0	73.3
	CMC 4	15.0	

3. Results and discussion

3.1. Reproducibility of ultrasonic degradation

The reproducibility of ultrasonic degradation was studied using four similar CMC polymer mixtures (Mix 4–7). It was seen that the viscosity of the solutions decreased equally in all the four cases (Fig. 1), and thus the ultrasonic degradation was reproducible. Also it was seen that the viscosity decreased rapidly during the first hour of ultrasonic treatment and the degradation was stabilised in 180 min. Thus the changes in dynamic viscosity were calculated at 180 min in this study. The stability of the viscosity reduction is detailed in earlier study [20].

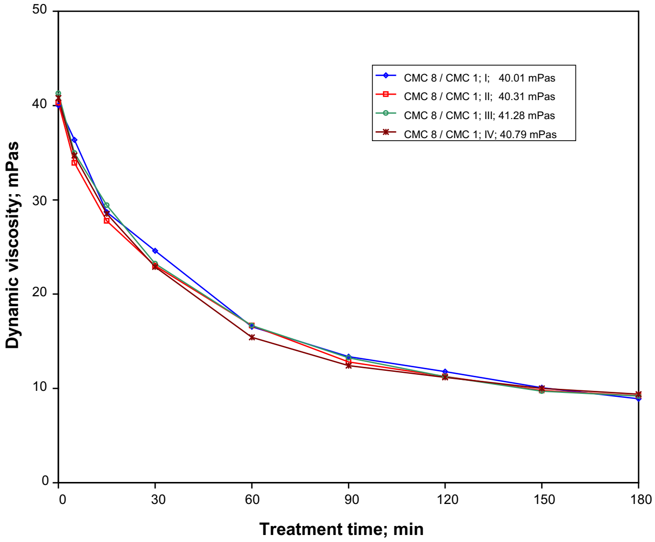

Fig. 1. Reproducibility of ultrasonic degradation of CMC polymer mixtures.

3.2. Effect of initial dynamic viscosity

The effect of the initial dynamic viscosity of a single CMC polymer or polymer mixtures on the change of dynamic viscosity was studied. The results showed that the higher was the initial dynamic viscosity the faster was the degradation. Also the change in 180 min was greater for the polymer mixtures with higher initial dynamic viscosity than the polymer mixtures with lower initial dynamic viscosity (Fig. 2). When the initial dynamic viscosity of the polymer mixtures was nearly the same the mixtures having polymers of higher molecular mass degraded faster than the mixtures having polymers of lower molecular mass (Fig. 2; CMC 5, CMC 6/2, CMC 6/3, CMC 6/4 and CMC 8/2).

In earlier studies it has been concluded that the increase in viscosity of the solution leads to decrease in degradation or that there is an optimum viscosity for degradation [1, pp. 115–117,11,15,18–20]. It is known that the formation of cavitation is more difficult to produce in viscous liquids. On the other hand, the effects resulting from cavitation

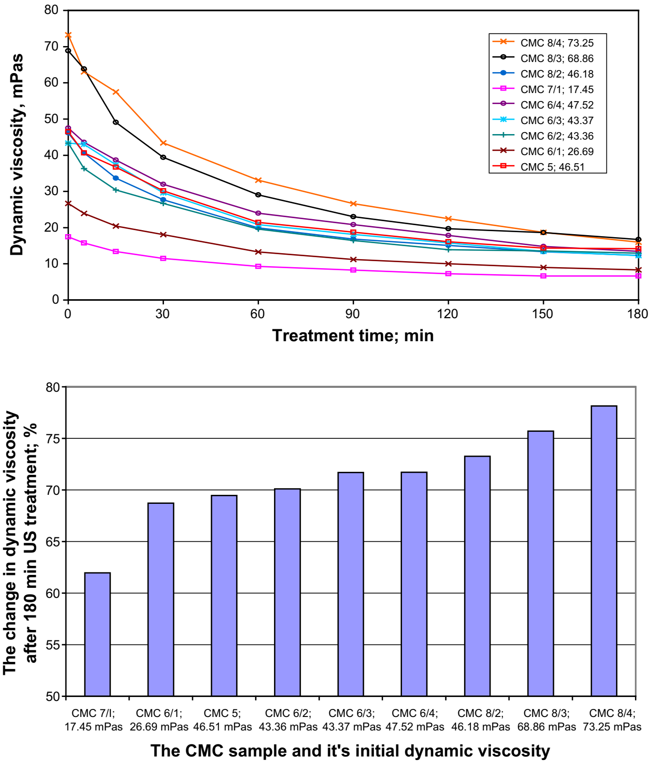

Fig. 2. Dynamic viscosities of the CMC polymer mixtures during ultrasound treatment (above). Effect of initial dynamic viscosities on the change in dynamic viscosities after 180 min ultrasound treatment (below).

collapse in viscous liquids are stronger than collapse in less viscous liquid [1, p. 107]. In this study the viscosities of polymer solutions were in the area where the efficiency of ultrasound was enough to overcome the natural cohesion forces acting within the liquid. The effects resulting from cavitation collapse in viscous liquids were stronger than collapse in less viscous liquids, and correspondingly stronger effects in viscous polymer mixtures caused faster degradation than in less viscous polymer mixtures. This is in agreement with general ultrasound theory although it is in disagreement with the other literature results told above [1, pp. 115–117,11,15,18–20]. Maybe in those studies the intensity of ultrasound has not been high enough to exceed the cavitation threshold in viscous liquids.

3.3. *Effect of molecular mass*

As told before it was impossible to adjust the initial dynamic viscosities of CMC polymer mixtures to the same level. Thus for the molecular mass studies PEG was chosen for viscosity adjustment. If the temperature was adjusted to 40 °C during ultrasound irradiation of PEG, ultrasound did not degrade PEG. If the temperature was allowed to increase up to 70 °C caused by ultrasonic irradiation, other ultrasonically assisted reactions like polymerization of PEG took place and the dynamic viscosity of PEG increased (Fig. 3).

The molecular mass studies showed that when the initial dynamic viscosities were adjusted to the same level using PEG the higher was the molecular mass of the polymer the larger was the change in dynamic viscosity after 180 min as can be seen in Fig. 4.

According to this examination the extent of degradation increased with increasing molecular mass of the CMC polymer. This study is in agreement with earlier studies where it has been found that with the largest molecules ultrasonic degradation was the fastest [2, pp. 156–157,19]. This observation strengthens the claim that ultrasonic degradation, unlike chemical or thermal decomposition, is a non-random process with cleavage taking place roughly at the centre of the molecule and the longer the molecule the faster the degradation [2, p. 156].

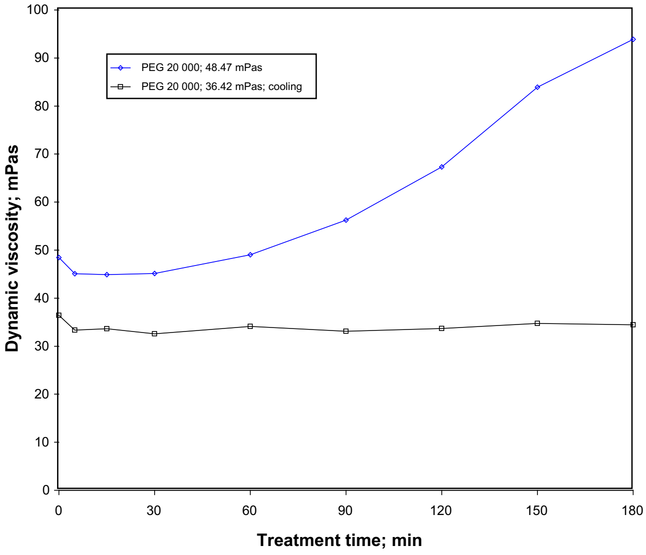

Fig. 3. Ultrasonic degradation of PEG with and without cooling.

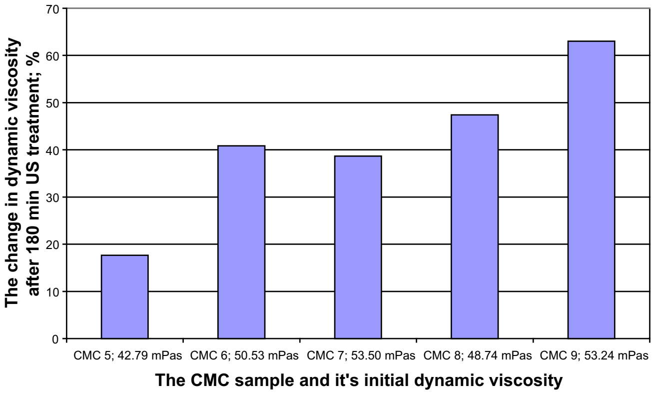

Fig. 4. Effect of molecular mass on the change in dynamic viscosities of CMC polymers after 180 min ultrasound treatment when the initial dynamic viscosity levels were similar.

3.4. *Effect of polymer concentration*

The effect of the solution concentration on the degradation has been investigated earlier in the literature so that the effect of the viscosity has not been separated from the concentration studies. As told above it has been found that the extent of degradation decreases with an increase in solution concentration or that there is an optimum polymer concentration for degradation (see Chapter 3.2).

In this study the concentration experiments were carried out at two viscosity levels (~35 mPas and ~400 mPas). The change of dynamic viscosity after 180 min ultrasound treatment was greater for the polymers with higher concentration than the polymers with lower concentration in both viscosity levels (Fig. 5). Thus, the high concentration

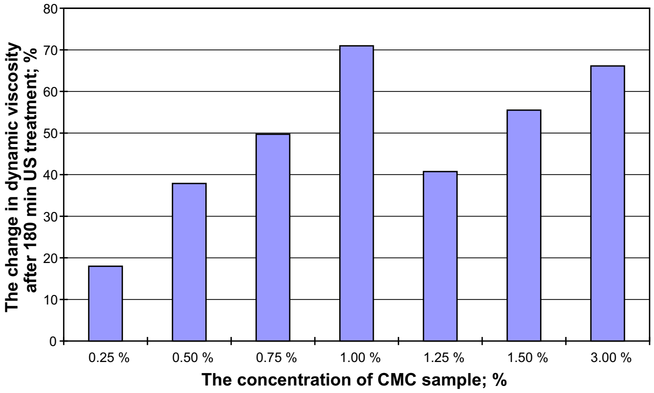

Fig. 5. Effect of polymer concentration on the change in dynamic viscosity of CMC polymer mixtures after 180 min ultrasound treatment. Experiments were carried out at two viscosity levels (~35 mPas and ~400 mPas).

enhanced the degradation extent. The results do not support the findings of other researchers [1, pp. 115–117,11,15,18–20]. The changes in dynamic viscosity in the area of 0.25–1.00% w/w differed from the area of 1.00 – 3.00% w/w because of the different initial dynamic viscosity levels.

When the only affecting factor is the concentration and not the concentration together with the viscosity it seems that the higher amount of polymer in aqueous liquid leads to the faster degradation. It may be so that there are more molecules to be degraded when the concentration is higher and that is why the degradation is faster.

4. Conclusions

In this study the effect of the initial dynamic viscosity, the molecular mass and the concentration of carboxymethylcellulose (CMC) polymers on the ultrasonic degradation were studied independently. In the cases where the initial dynamic viscosities of polymer solutions are not at the same level the sonolytic degradation of CMC polymer is mainly depended on the initial dynamic viscosity. The higher is the initial dynamic viscosity the faster is the degradation. This is in agreement with the ultrasound theory, because the effects resulting from the cavitation collapse in viscous liquids are stronger than the collapse in less viscous liquid. The study showed also that when the initial dynamic viscosities are adjusted using polyethyleneglycol (PEG) the higher was the molecular mass of CMC polymer the faster was the degradation. This is also in agreement with earlier studies, where it has been found that the larger the molecule the faster the degradation [2, pp. 156–157,19]. The CMC concentration studies proved that the higher the polymer concentration the higher the degradation when the initial dynamic viscosity is adjusted using PEG. This is in disagreement with the earlier studies where the degradation decreased with an increase in solution concentration [1, pp. 115–117,11,15,18–20]. However, in those earlier studies the viscosity was not adjusted, being it, according to this study the main parameter in polymer degradation.

Acknowledgements

The authors thank TEKES, the National Technology Agency of Finland and VTT for their financial support.

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Article IV

Ultrasound assisted method to increase soluble chemical oxygen demand (SCOD) of sewage sludge for digestion

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Ultrasound assisted method to increase soluble chemical oxygen demand (SCOD) of sewage sludge for digestion

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Abstract

The aim of this study was to clarify the possibilities to increase the amount of soluble chemical oxygen demand (SCOD) and methane production of sludge using ultrasound technologies with and without oxidising agents. The study was done using multivariate data analyses. The most important factors affected were discovered. Ultrasonically assisted disintegration increased clearly the amount of SCOD of sludge. Also more methane was produced from treated sludge in anaerobic batch assays compared to the sludge with no ultrasonic treatment. Multivariate data analysis showed that ultrasonic power, dry solid content of sludge (DS), sludge temperature and ultrasonic treatment time have the most significant effect on the disintegration. It was also observed that in the reactor studied energy efficiency with high ultrasound power together with short treatment time was higher than with low ultrasound power with long treatment time. When oxidising agents were used together with ultrasound no increase in SCOD was achieved compared the ultrasonic treatment alone and only a slight increase in total organic carbon of sludge was observed. However, no enhancement in methane production was observed when using oxidising agents together with ultrasound compared the ultrasonic treatment alone. Ultrasound propagation is an important factor in ultrasonic reactor scale up. Ultrasound efficiency rose linearly with input power in sludge at small distances from the transducer. Instead, ultrasound efficiency started even to decrease with input power at long distances from the transducer.

Keywords: Ultrasound; Soluble Chemical Oxygen Demand (SCOD); Sludge disintegration; Oxidising agents; Anaerobic digestion

1. Introduction

Large quantities of sludge are produced in biological wastewater treatment. Sludge is highly putrescible and therefore it has to be stabilised in order to enable an environmentally safe utilization or disposal. The anaerobic digestion is the standard technique to stabilise the sludge. Digestion produces biogas and reduces the amount of organic matter [1]. Due to the rate-limiting step of biological sludge hydrolysis anaerobic degradation is a slow process and large fermenters are necessary. Typical digestion times are 20 or more days. The degree of degradation of organic matter varies between 25% and 60%. Reduction of volatile solids is more pronounced in digestion of primary sludge as compared to the digestion of secondary sludge [2].

Ultrasound assisted sludge degradation has been extensively studied in the recent 10 years in laboratory-, pilot- and recently also in full scale. Ultrasonical sludge disruption releases soluble organic cell compounds into the aqueous phase, which produce more biogas in digestion. Studies have indicated, that especially particularly low (20 kHz) frequency ultrasound

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and relative high ultrasonic intensity are well suited for the disintegration of sewage sludge [2,3]. This is attributed to high mechanical shear forces by jet streams during cavitation bubble implosion [1]. Sonication of secondary sludge results in a more pronounced release of chemical oxygen demand as compared to raw sludge treatment. The solids concentration of sludge affects the disintegration efficiency [2]. Very few articles handling chemical pretreatment of sludge together with ultrasound before anaerobic digestion are published. It has been reported that disintegration of sludge was enhanced when NaOH together with ultrasound was used [4].

The aim of this study was to find out the possibilities to increase the amount of SCOD and methane production of sludge using ultrasound technologies with and without oxidising agents. The study was done using multivariate data analyses.

2. Experiments

2.1. Ultrasonic reactors, multivariate data analysis and the propagation of ultrasound in sludge

Two kinds of ultrasonic reactors made by VTT Processes were used. The most of the experiments were done with 10 l round steel batch reactors operating at 22–27 or 40 kHz frequencies. The reactors comprise of a function generator Tabor Electronics 8553 or AMREL Model FG-506, a power amplifier ENI Model 1140LA-1331 and a lab mixer IKA EUROSTAR digital. The second ultrasonic device was 27 kHz rectangular batch reactor with IEC US-1200A ultrasonic generator (Fig. 1). The volume of the second reactor can be changed.

Using Unscrambler-multivariate data analyses program the effect of ultrasonic power, ultrasonic frequency, DS of the sludge, mixing of sludge, temperature of the sludge and ultrasonic treatment time on SCOD was studied. The experiments were carried out in round batch reactors. Twofold factor method and Box Behnken—program were used to design experiments and PLS-1 method was used to analyse the results. SCOD was response variable in both the cases. The values of variables are shown in Tables 1 and 2.

The propagation studies were done using hydrophone (Reson 199010) and the visual effect of ultrasound was studied using aluminium foil. The propagation experiments were carried out in the rectangular batch reactor.

2.2. Sludge and methane production assays

Excess sludge from Nenäinniemi wastewater treatment plant, in Jyväskylä, Finland, was used. The extent of cell disintegration of excess sludge was determined as an increase of the SCOD in the sludge supernatant. The supernatant for SCOD analyses before and after ultrasonic treatment of sludge was obtained by high-speed centrifugation (30 min, 3023*G*). Sludge samples were preserved using 4-M sulphuric acid before SCOD analyses. The SCOD analyses were done using Hach DR/2000 Spectrofotometer.

Methane production assays were performed using 120-ml serum vials. After adding the inoculum (5 ml) and studied material (20–30 ml), distilled water was added to obtain the final liquid volume of 60 ml. The inoculum was mesophilically digested sewage sludge (TS 2.2%, VS/TS 0.56) from Nenäinniemi wastewater treatment plant. Total Solids (TS) and Volatile Solids (VS) were analysed according to Finnish standards (SFS 3008). The pH of the inoculum and studied untreated and ultrasound treated sludge samples were 6.9–7.3. Vials with inoculum and without added material were assayed to subtract inoculum's methane production from the studied sludge. The content of the

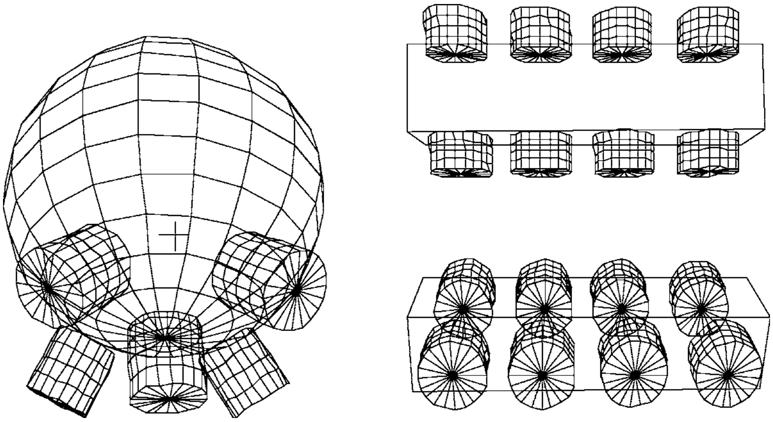

Fig. 1. On the left the scheme of round steel batch reactor having 5 Langevin type transducers and on the right the scheme of rectangular batch reactor having 8 Langevin type transducers.

Table 1
Values and results of the five variables when using twofold factor method in experiment design and PLS 1—method in result analyses

Variable	Levels	SCOD
US power	100 or 200 W/l	++
US frequency	22 or 40 kHz	NS
DS of sludge	0.9% or 2.4%	++
Mixing of sludge	200 or 500 rpm	NS
Temperature of sludge	20 or 40 °C	++

NS = no significant meaning; − = the bigger value has a negative effect; + = the bigger value has a positive effect.

Table 2
Values and results of the three variables when using Box Behnken—program in experiment design and PLS 1—method in result analyses

Variable	Levels	SCOD
Treatment time (A)	5, 17.5 or 30 min	+++
US power (B)	50, 175 or 300 W/l	++
DS of sludge (C)	0.8%, 1.6% or 2.5%	++
A and B together		++
A and C together		NS
B and C together		+

NS = no significant meaning; − = the bigger value has a negative effect; + = the bigger value has a positive effect.

vial was flushed with nitrogen to remove oxygen, and the vials were sealed with butyl rubber stoppers and aluminium crimps. The methane production assays were carried on 19 days in 35 °C. Gas chromatograph Perkin Elmer Autosystem XL was used to determine the methane content of the biogas.

2.3. Oxidising experiments

Oxidising experiments were carried out in the 22–27 kHz round batch reactor with mixer using peracetic acid (CH_3CO_3H) and hydrogen peroxide (H_2O_2) as oxidising agents. The concentration of peracetic acid was 38–40% and 50% for hydrogen peroxide. The amount of peracetic acid varied in the range of 4–20 and 25–70 kg/t DS for hydrogen peroxide. The incubation time varied from 10 to 20 min. The oxidising agents were added into sludge before, during or after ultrasound disintegration. The temperature before the incubation of oxidising agents was 14 ± 2 °C. Pure oxidising treatment increased temperature 3 °C while ultrasound treatment increased temperature 4–16 °C depending on treatment time. SCOD and total organic carbon (TOC) were used to study the effect of oxidising agents on disintegration of sludge. TOC analyses were done using Shimadzu Total Organic Carbon Analyzer TOC 5000A. Sample preparation for the TOC analyses were carried out using the same method as for the SCOD analyses except TOC samples were also filtered using GF50 filter paper.

3. Results and discussion

3.1. Multivariate data analysis and SCOD

Ultrasonic power, DS of sludge and ultrasonic treatment time (Tables 1 and 2) had an obvious effect on the disintegration of excess sludge. The largest SCOD increase was obtained with the highest power, highest DS and longest treatment time used, which agrees with the studies published earlier. This study showed that also the temperature of sludge is an important parameter in ultrasonic disintegration.

Disintegration of sludge presupposes high mechanical shear forces caused by jet streams during cavitation bubble implosion. That is why disintegration requires high ultrasonic power. However, the optimisation of energy consumption is essential in ultrasonic assisted disintegration. Thus the common effect of power and treatment time was studied further. Larger SCOD increase was obtained with same energy consumption when using high ultrasonic power together with short treatment time as when using low ultrasound power with long treatment time (Fig. 2).

SCOD was observed to increase with sludge DS due to the higher concentration of microbes that could be disrupted. However, every ultrasonic reactor has the characteristic maximum DS to enable ultrasonic wave propagation and cell disintegration. The factors limiting this maximum DS value are for example reactor size, transducer type, viscosity of sludge, temperature of sludge and polymer concentration if polymers are added in flocculation.

Multivariate data analysis showed that disintegration was enhanced with treatment temperature. In more accurate experiments temperature was adjusted during the treatment with and without ultrasound (Fig. 3). Heating increased the amount of SCOD. However,

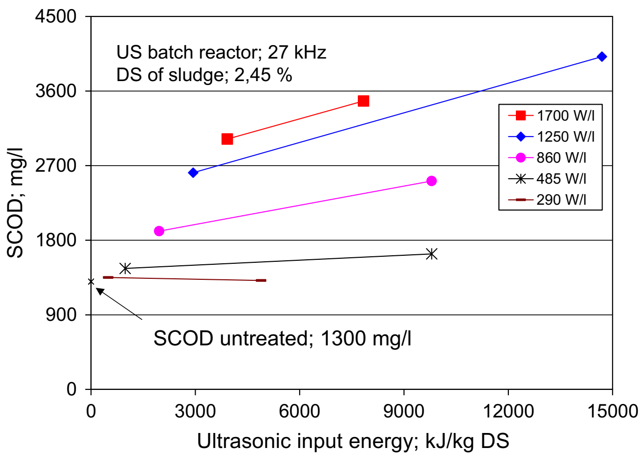

Fig. 2. The effect of ultrasonic energy on SCOD when different ultrasonic efficiencies were used.

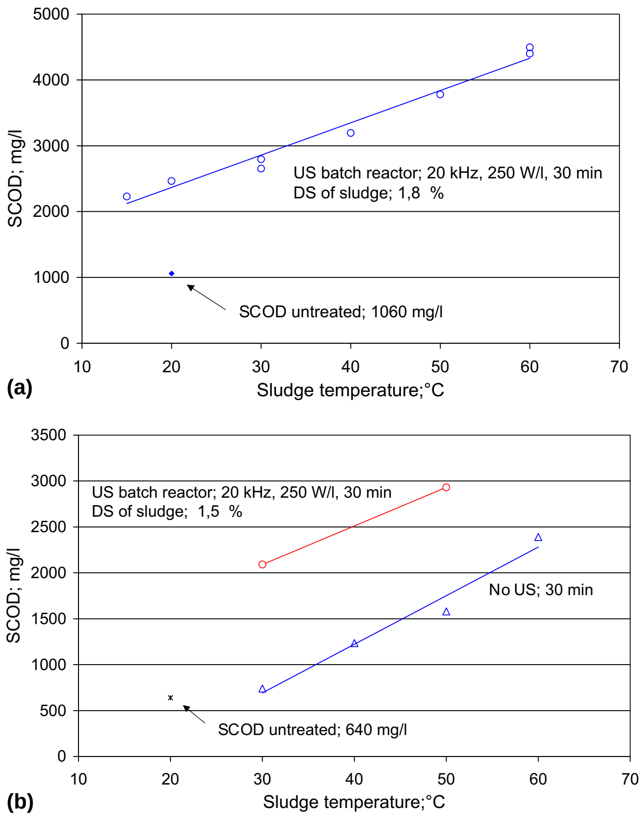

Fig. 3. (a) SCOD values as a function of sludge temperature in the experiments with ultrasound. (b) SCOD values in different sludge temperature without ultrasound. Ultrasound experiments using same sludge were used as reference points.

larger increases in SCOD were obtained with ultrasound than with heating alone.

The ultrasonic frequencies and mixing rates used did not affect on SCOD. However, the studied parameter values were so close to each other that the effects did not become clear.

3.2. The effect of ultrasound treatment on methane production

The effects of 2.5 and 10 min ultrasound treatment (27 kHz, 200 W/l) on the methane production of the filtrated fraction of excess sludge were studied in methane production assays using untreated sample as a control. The longer the treatment time the higher was the initial SCOD in the beginning of the assays. With all the samples, methane production started without any delay. During the 19 days assays, methane productions were 8–17 times higher for the treated samples than for the untreated samples. Methane production per kilogram of SCOD in the sample was same for 2.5 and 10 min treated samples suggesting that SCOD in these samples was equally degradable despite differences in its quantities (Table 3).

Anaerobic batch studies were also performed with 20 differently treated samples of excess sludge. The ultrasound power ranged up to 300 W/l and the treatment times up to 30 min while sludge TS ranged from 0.6% to 2.5%. The sludges used in experiments were obtained in four different times from the plant. The effects of various treatments on methane production varied without clear trend. In some cases the same treatment increased the methane production with one sample, but decreased with another. However, in most assays 10–20% more methane was obtained from treated sludge compared to untreated sludge, while in some case treatments resulted in slight decrease of methane production. In general, the higher the SCOD after the treatment the more methane was produced. These results suggest that ultrasound treatment must be optimised separately in each application.

3.3. Oxidising measurements

When studying the effect of the hydrogen peroxide or peracetic acid on the ultrasonically assisted sludge disintegration SCOD results showed that no increase in SCOD was achieved when using ultrasound together with oxidising agents compared the ultrasonic treatment alone. There was no difference whether oxidising agents were added before, during or after ultrasonic treatment. Pure oxidising agents had a slight positive effect on SCOD but the effect was minor compared the effect of ultrasonic treatment (Fig. 4a). The result could not be improved when prolonging the incubation time or increasing the dosage of oxidising agent in the circumstances studied. The increase of oxidising agent dosage even decreased SCOD of sludge (Fig 4a). On the contrary TOC results showed that peracetic acid has a slight effect on ultrasonically assisted sludge disintegration (Fig. 4b). However, no enhancement in methane production was noticed. When oxidising agents disintegrate sludge, they at the same time destroy the organic matter produced. This and perhaps wrong oxidising agent

Table 3
The effects of ultrasound treatments on the SCOD of excess sludge and on the methane production of filtrate of excess sludge in batch assays during 19 days

Sample	SCOD, mg/l	Methane production, ml	Methane production, m^3/m^3 of sample	Methane production, m^3/kg SCOD in sample
Untreated	620	2	0.07	3.22
2.5 min	2100	17	0.56	8.09
10 min	4200	34	1.13	8.09

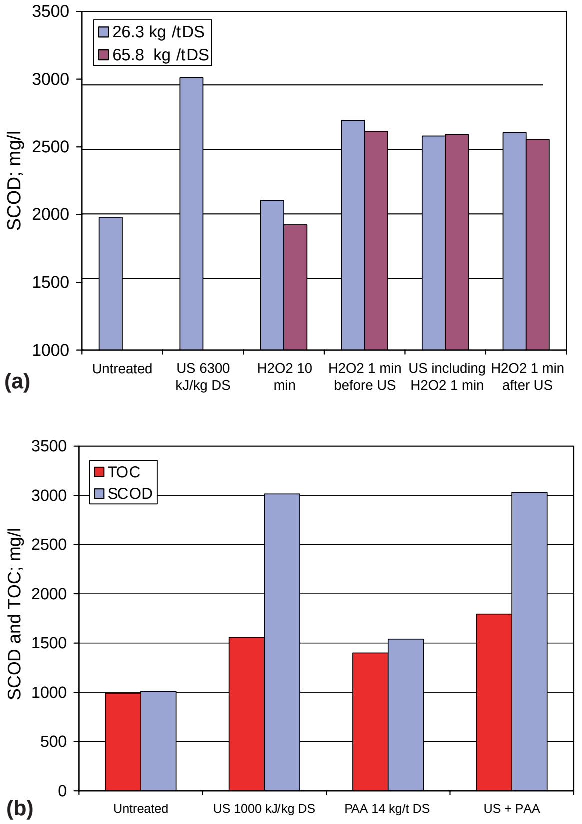

Fig. 4. (a) SCOD content in sludge when using hydrogen peroxide as an oxidising agent. (b) SCOD and TOC content in sludge supernatants when using peracetic acid as on oxidising agent.

dosage (Fig. 4a) might be the reasons for a minor effect on the oxidising results or methane production. The effect of the oxidising agents on the sludge and the ultrasonically assisted sludge disintegration is complex and needs further investigations.

3.4. The propagation of ultrasonic waves in sludge

Ultrasound propagation from the transducer is important to know when scaling up ultrasonic reactors. Ultrasonic propagation was measured by hydrophone. Hydrophone value increased linearly as a function of ultrasonic input power at small sludge thickness (DS 2.3%) in front off the transducer. When the sludge thickness was 4 cm or more, hydrophone value started even to decrease when 400 W input power was exceeded due to poor propagation of ultrasound (Fig. 5). When the ultrasonic power was high cavitation bubbles appeared only at the vicinity of the transducer. This phenomenon also causes the cavitation erosion of the transducer surface. Propagation of ultrasound can be altered with sufficient mixing or flow. High power was found to disintegrate sludge efficiently (see Section 3.1). Thus, input power and propagation of ultrasound in sludge should be optimised when designing ultrasonic reactors for sludge disintegration.

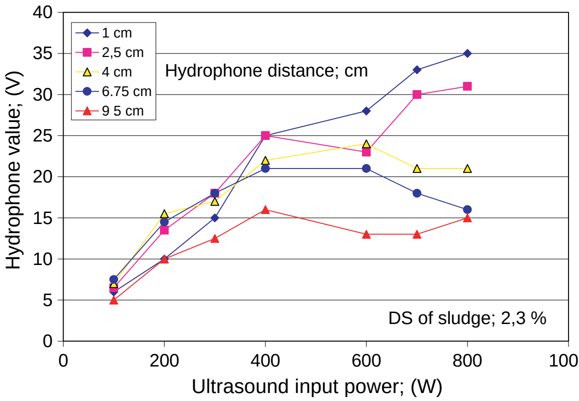

Fig. 5. The propagation studies of ultrasound using hydrophone.

The visual effect of ultrasound inside the rectangular reactor was also studied using aluminium foil. These experiments showed the periodic and local nature of ultrasonic cavitation. For example more holes caused by cavitation was formed to the aluminium foil located 13.5 cm than 6 cm from the transducer while it was on the contrary in the case of 14.5 and 5 cm (Fig. 6).

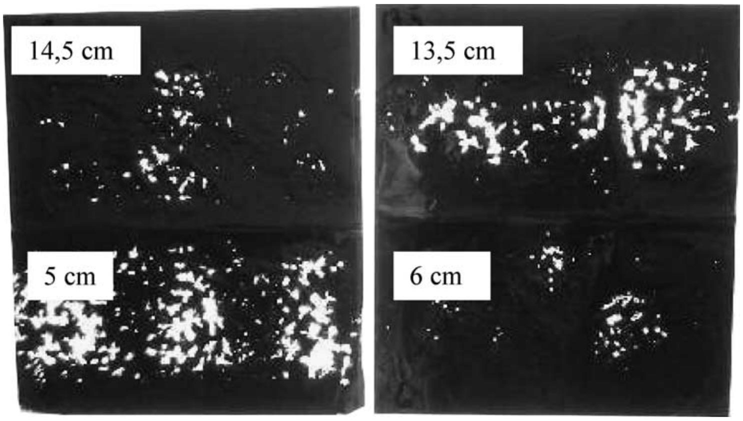

Fig. 6. The visual studies of ultrasound using aluminium foil.

4. Conclusions

Ultrasonic disintegration of sludge increased the amount of SCOD and methane production. The multivariate data analysis showed that ultrasonic power, DS of sludge, sludge temperature and ultrasonic treatment time affect significantly on the sludge disintegration. It was also observed that high ultrasound power together with short treatment time is more efficient than low ultrasound power with long treatment time. When using oxidising agents together with ultrasonic disintegration there was no increase in SCOD and only a slight increase in TOC compared the ultrasonic treatment alone. However when using oxidising agents together with ultrasound, no enhancement in methane production was observed. Ultrasound propagation is an important factor in ultrasonic reactor scale up. Ultrasound efficiency rose linearly with input power in sludge at small distances from the transducer. Instead, ultrasound efficiency started even to decrease with input power at long distances from the transducer.

Acknowledgment

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Article V

Ultrasonically aided mineral processing technique for remediation of soil contaminated by heavy metals

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Ultrasonically aided mineral processing technique for remediation of soil contaminated by heavy metals

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Abstract

In this study, power ultrasound was used as aiding method for the mineral processing technique, which have recently been developed for the remediation of soil contaminated by heavy metal containing bullets, their broken parts and alteration products. Power ultrasound was used to disperse the soil to remove metals and metal compounds from soil particle surfaces instead of attrition conditioning. The soil diluted with water was treated using 22 kHz ultrasound power of 100 W up to 500 W. The effect of different ultrasonic treatment time and pulsation of ultrasound were studied on the purity of sink and float fractions in heavy medium separation process, screen fractions, and mineral concentrates and tailings from flotation process. Ultrasound enhanced the remediation of soil fractions in all the studied cases. Optimisation of the ultrasonic power will be done in the continuation study.

Keywords: Ultrasound; Remediation; Soil; Heavy metals; Mineral processing

1. Background

Separation techniques used in mining industry, such as screening, heavy medium separation and flotation, have recently been successfully applied in the remediation of soils contaminated by heavy metal like bullets, their broken parts and alteration products [3–5]. Soil remediation using mineral processing methods aided by power ultrasound is a novel method, where the effects of power ultrasound were used to further improve the operation of these mineral processing techniques. The ultrasound was used instead of attrition conditioning, it was expected to produce less fine material than the traditional methods. The power ultrasonic effects are based mainly on liquid cavitation, which creates extremely strong liquid jets against particle surfaces [6]. There are some studies where power ultrasound is successfully used for cleaning of different particle surfaces from organic or inorganic matter [1,2,7–10]. There is also one commercial remediation technique, where ultrasound has been used as aiding technique. The vibrating tray (Advanced Sonic Processing Systems, USA) using 20 kHz magnetostrictive transducers resembles most the technique under developing. The aim is to clean particle surfaces, like ore, ash or soil, from agents in order to make the sludge more reactive for chemicals.

In the technique studied power ultrasound was mainly used to aid removing metals and metal compounds from soil particle surfaces. The aim was to decrease the heavy metal content of remediated soil under limit values for problem waste (Table 1) using the new remediation process. So the remediated soil could be left to their original place. The remediation process is more competitive without transportation of large amounts of material.

2. Experimental

The soil examined was brought from former military shooting range. The coarsest material (+20 mm), which did not contain bullets or their parts, was screened out before ultrasonic treatment experiments. The other

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Table 1
Limit values for heavy metals in contaminated soils in Finland (originated from shooting range)

	Limit values for contaminated soils (mg/kg)		Limit values for problem waste (mg/kg)
	Lower limit	Higher limit	
Cu	15	400	2500
Pb	10	300	2500

screen fractions −20 to +4 mm, −4 to +1 mm, −1 mm and −250 μm (particles smaller than 250 μm) containing heavy metals were treated separately into remediation process using now ultrasound treatment before separations.

A round shaped ultrasonic reactor of 10 l was used in each batch experiments. It contained five 22 kHz piezo ceramic transducers on the bottom of the reactor. Ultrasonic frequency and power were adjusted using ENI 1140 LA (S/N 563) power amplifier and Tabor 8552 function generator (Table 2, experiments 1–10) or IEC US1200 ultrasonic generator (Table 2, experiments 11–26). The used ultrasonic equipments are presented in the Fig. 1.

The input power of 100 W up to 500 W was used in the experiments. The effect of different treatment time and pulsation of ultrasound were studied on the remediation of different soil fractions. The soil was diluted with water for the experiments and mixed during ultrasonic treatment using agitator rotations of 150–200

Fig. 1. Ultrasonic equipment: reactor with mixer, power amplifier, function generator and impedance adapter.

Table 2
Conditions of ultrasonic treatment in each experiment

Experiment	Soil/kg	Water/kg	Power/W	Treatment time/min	Pulsation (on/off 0.5 s)
Experiment 1[a]	1	5	250	60	No
Experiment 2[a]	1	5	500	30	No
Experiment 3[a]	1	5	–	–	–
1	0.75	1.25	250	60	No
2	0.75	1.25	250	15	No
3	0.75	1.25	250	5	No
4	0.75	1.25	–	–	–
5–6	0.75	1.25	250	30	No
7	0.75	1.25	250	15	No
8	0.75	1.25	250	15	No
9	0.75	1.25	–	–	–
11[b]	0.35	2	250	15	No
12[b]	0.4	2	250	15	No
13	0.58	1.74	100	5	No
14	0.58	1.74	100	5	Yes
15	0.58	1.74	100	0.5	No
16	0.58	1.74	250	5	No
17	0.58	1.74	250	5	Yes
18	0.58	1.74	250	2.5	No
19	0.58	1.74	250	0.5	No
20	0.58[c]	1.74	400	5	Yes
21	0.58	1.74	–	–	–
22	0.58	1.74	250	5	No
23	0.58	1.74	250	5	No
24	0.58	1.74	–	–	–
25	0.29	1.74	250	2.5	No
26	0.58	1.74	–	–	–

[a] Experiments 11.06.02.
[b] NA.
[c] Sludge mass was 2.524 kg.

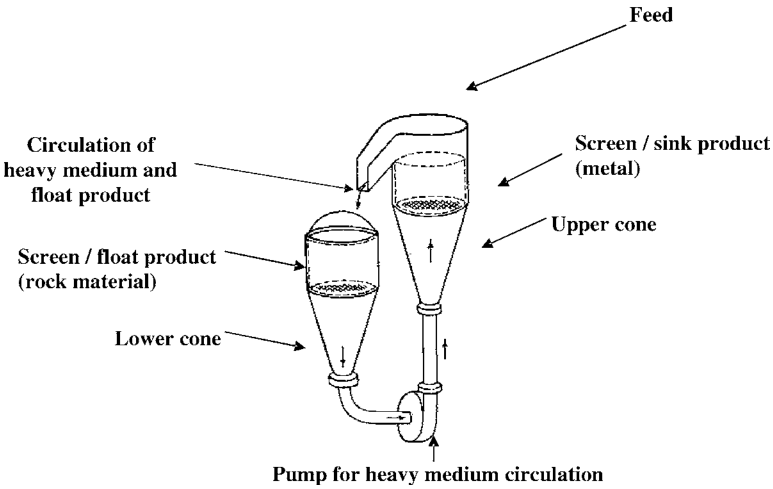

Fig. 2. Laboratory scale heavy medium separation apparatus (Erickson's cones).

per minute. The treatment conditions are shown in Table 2.

Contaminated soil fractions of −20 to +4 mm and −4 to +1 mm were treated separately using ultrasound before heavy medium separation tests. Reference tests for each test were made using the same procedure without ultrasound. The sink and float fractions from heavy medium separation were analysed using XRF-method. The laboratory scale apparatus used in heavy medium tests, Erickson's cones, is presented in Fig. 2. The density of heavy medium used in the tests was about 3.1–3.2 kg/dm^3 and suspension was prepared by mixing water and ferrosilicon. In these conditions the stones could be recovered into the float product and bullets same as their broken parts into sink product when heavy medium was circulated by pumping. Contaminated soil was fed into the upper cone. The tests were carried out as batch experiments.

Ultrasonically treated −1 mm fraction was screened into eight smaller fractions and the metal content (lead and copper) in each fraction was analysed using XRF-method.

The fraction of −1 mm was at first screened to the fractions of +250 and −250 μm before flotation and US treatment. Flotation experiments were done only for the fraction of −250 μm because the flotation method used could not effectively operate with +250 μm particles. This lack will be avoided in the continuation study by using SIF (flotation in froth) technology, which can operate with −1mm material. Soil fraction of −250 μm was first treated using ultrasound with different combinations of treatment time and pulsation, and then floated. Mineral concentrates and tailings from flotation were filtrated and metal contents (lead and copper) were analysed by XRF-method from the filter cakes. The flotation experiments were carried out using mainly fatty acid type collector (RaRa = turnip fatty acid). Emulgator type KOAL 10 was used to disperse fatty acid collector to water to obtain higher effect in collection of hydrophobic particles. Sulfid collector (KAX = K-amyl xanthate) was used in some experiments alone or together with $CuSO_4$-activator. The purpose of this activator was to change particle surface properties by changing for example the original Pb-compound to corresponding Cu-compound, which could make collection of particles better. NaHS-activator was also used in some experiments together with sulfid collector (NaIPX = Na-isopropyl xanthate). The purpose of NaHS treatment was to modify the surface of the particles to be flotated to the corresponding heavy metal sulfids in which state they can easier be flotated than in their original form of heavy metal carbonate or pure heavy metal. NaOH (fatty acid flotation) and H_2SO_4 (xanthate flotation) were used for pH regulation.

3. Results

In heavy medium separation the ultrasonic pretreatment experiments (experiments 1–3, Table 2) decreased lead (Pb) content in float product of the −4 to +1 mm fraction (rock material) from 0.47% at least to 0.15% (Fig. 3). Lead recovery into the same product decreased correspondingly from 0.75% at least to 0.3%. In −20 to +4 mm fraction the lead content decreased from 0.17% at least to 0.06%. The decrease in copper content was smaller in the remediated soil. Visual picture of the purification degree of metal (sink) and rock material (float) fractions is presented in Fig. 4.

The ultrasonic treatment of the fine test material (−1 mm) (experiments 5–6, Table 2) caused a transition in the lead contents of the screen fractions. The lead contents lowered by the treatment in all other fractions except the finest (−32 μm) fraction (Fig. 5). Copper content had the similar trend as lead content. The reason could be the accumulation of separated Pb and Cu to the finest fraction and uneffective US cleaning with this fraction. Swamy and Narayana have shown with CuO ore leaching experiments that 45 μm is the critical grain size, below which application of US is not effective.

In the first flotation tests, when fatty acid was used as collector chemical (Fig. 6, experiments 1–4, Table 2) the lead content decreased in the remediated soil from 0.79% to 0.76% (refuse ore in enrichment process) using fifteen minutes ultrasonic treatment. When five minutes ultrasonic treatment was used lead content decreased even to 0.69% (Fig. 6, experiment 3). If too long (60 min) ultrasonic treatment was used the lead content increased slightly. In flotation tests, when sulphide collector was used (experiments 7–9), the residual contents of heavy metals were much higher. However, ultrasound treatment decreased metal contents slightly also in these experiments. Experiments 13–26 (Fig. 7) were carried out using lower ultrasonic power, shorter treatment time and treatment pulsation. In these experiments effect of ultrasound were not very significant. Ultrasonic treatments were perhaps too weak compared to the earlier experiments (Fig. 6), where also the original metal concentration was much higher. Xanthate flotation together with $CuSO_4$ activator gave the weakest results. Xanthate flotation after sulfide treatment gave the best results. Only marginal fluctuations were obtained in the fatty acid flotation experiments. Thus, further research is needed to see how metal compounds and rock material are bound together, how US effects this binding

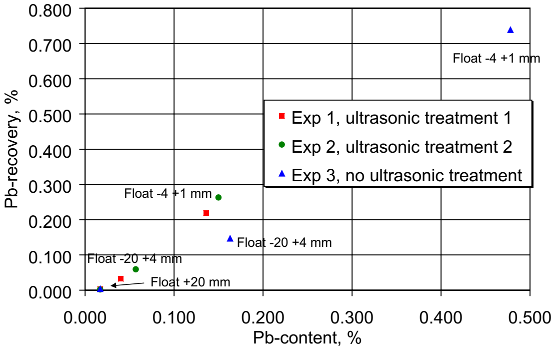

Fig. 3. Results from heavy medium separation tests for different screen fraction.

Fig. 4. End products of sink-float process (left sink product, right float product).

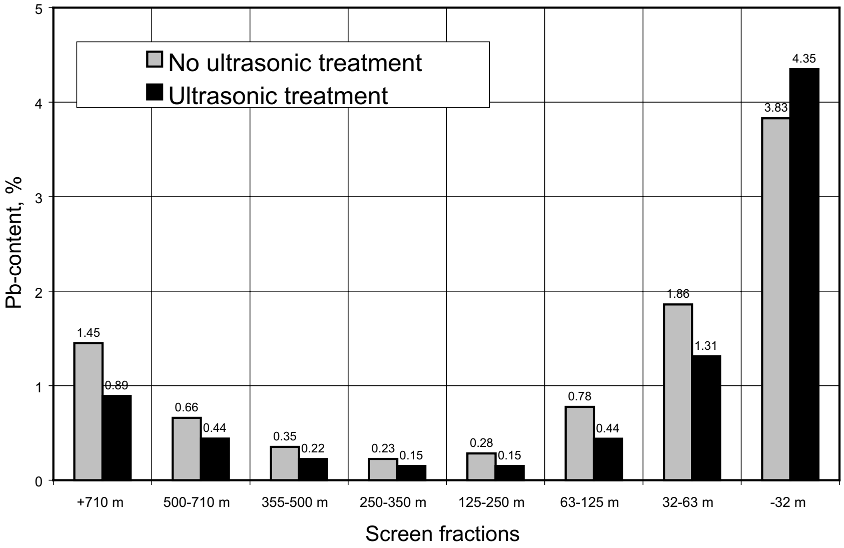

Fig. 5. Change of lead contents in material fractions caused by the ultrasound treating.

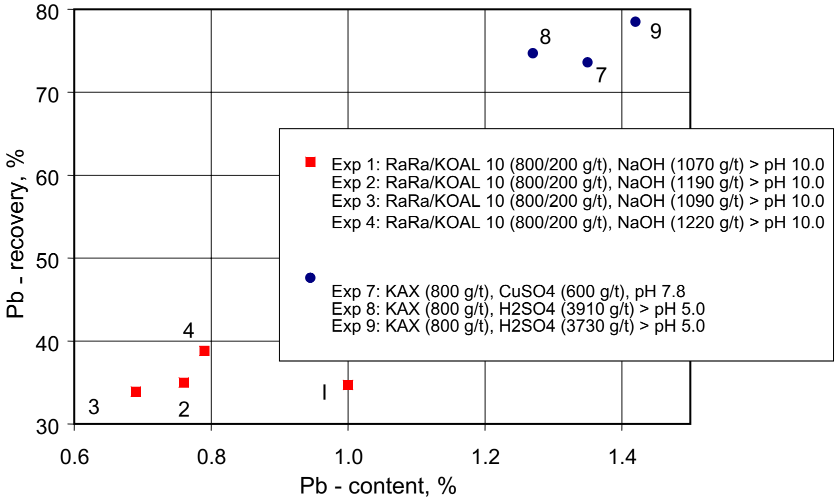

Fig. 6. Results of the flotation experiments for the fine soil fractions (−250 μm) (cleaned soil) at higher ultrasonic power. Experiments 4 and 9 are reference cases without US treatment.

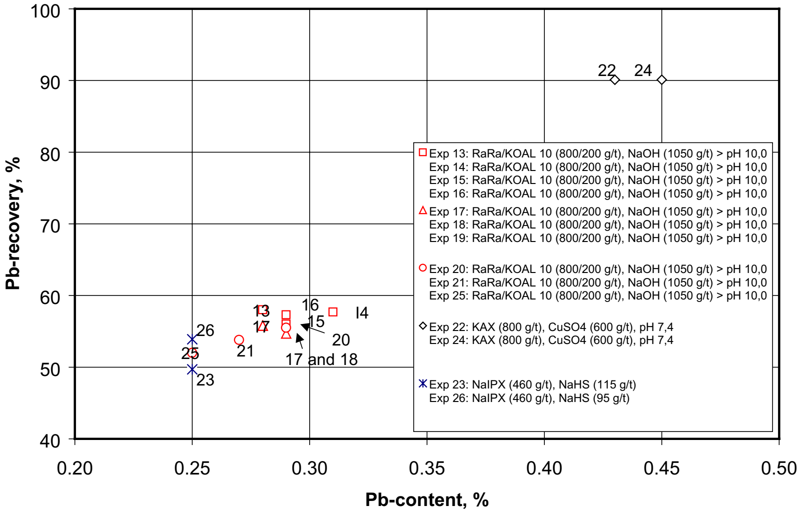

Fig. 7. Results of the flotation experiments for the fine soil fractions (−250 μm) (cleaned soil) at lower ultrasonic power. Experiments 21, 24 and 26 are reference cases without US treatment.

mechanism and to find out the right flotation conditions.

4. Conclusions

Ultrasound improved the remediation results of both products (sink and float products) in heavy medium separation. That was based on the fact that the amount of ultra fine metal fraction was diminished when attrition conditioning was replaced by ultrasound. The remediation process produced float product (cleaned soil) that could be left to their original place. This way the process costs would be lower without transportation of large amounts of soil materials.

The next phase is to study in more detail especially ultrasonic cleaning of the finer fraction (−1 mm) combined together with SIF flotation technology (separation in froth). SIF process can handle coarser fraction than conventional flotation technologies, which can handle materials up to the grain size of 250 μm. SIF technique is more economic new flotation method and combining it with ultrasonic treatment could make the total process commercially more interesting.

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Author(s)
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Title

Ultrasonically Enhanced Disintegration

Polymers, Sludge, and Contaminated Soil

Abstract

There are a great variety of potential applications of high–intensity ultrasonic energy. Of these, cleaning, plastic pounding, and at present also sludge disintegration and the remediation of contaminated soil are probably the best known and offer the most general market for high-intensity ultrasonics. All developments within the area of ultrasound applications lead to the creation of environmentally friendly processes and compounds, emphasizing the role of ultrasound in "green chemistry". Ultrasound technology is considered not easy to use in industrial processes, since devices providing high sonic energy are not easy to construct. This thesis investigates on a semi-pilot scale if it is possible to enhance the disintegration of three quite different samples: polymers, sludge, and contaminated soil by using ultrasound.

The results indicate that it is possible to enhance the disintegration of polymers by means of ultrasonic power only when the cavitation threshold is exceeded. Above the cavitation threshold, the most extensive degradation took place at the lowest ultrasonic frequency used. The biggest decrease (from 115,000 g/mol to 30,000 g/mol) in relative molecular mass (RMM) was observed when the concentration of polyvinyl alcohol (PVA) was the lowest (1.0%). However, in the case of carboxymethylcellulose (CMC) it was observed that when viscosity was not adjusted there is an optimum polymer concentration (1.5–2.0%) where degradation is most efficient. The thesis shows that the extent of ultrasonic depolymerization decreases with decreasing molecular mass of the CMC polymer. The study also reveals that ultrasonic irradiation causes narrowing of the molecular mass distribution. The degradation of CMC polymer proceeded linearly and the rate of ultrasonic depolymerization decreased with decreasing molecular mass. In cases where the initial dynamic viscosities of polymer solutions were not the same, the sonolytic degradation of CMC polymer mainly depended on the initial dynamic viscosity. The higher the initial dynamic viscosity, the faster the degradation. This work confirms the general assumption that the shear forces generated by the rapid motion of the solvent following cavitational collapse are responsible for the breakage of the chemical bonds within the polymer. The effect of polymer concentration could be interpreted in terms of the increase in viscosity with concentration, causing the molecules to become less mobile in solution with smaller velocity gradients around collapsing bubbles.

Ultrasonic disintegration of sludge increased the amount of soluble chemical oxygen demand (SCOD) and the production of methane. Multivariate data analysis suggested that ultrasonic power, sludge dry solids (DS), sludge temperature, and ultrasonic treatment time significantly affect sludge disintegration. It was also found that high ultrasound power together with a short treatment time is more efficient than low ultrasound power with a long treatment time. When using high ultrasound power, the ultrasound propagation is an important factor both in cavitation erosion prevention and reactor scale-up. Ultrasound efficiency rose linearly with input power in sludge at small distances from the transducer. On the other hand, ultrasound efficiency started even to decrease with input power at long distances from the transducer. When using oxidizing agents together with ultrasonic disintegration there was no increase in SCOD and only a slight increase in total organic carbon (TOC) compared to ultrasonic treatment alone. However, when using oxidizing agents together with ultrasound, no enhancement in methane production was observed.

Ultrasound improved the remediation results of both products (sink and float products) in heavy medium separation. This phenomenom was based on the fact that the amount of ultrafine metal fraction was diminished when attrition conditioning was replaced by ultrasound. The remediation process produced float product (cleaned soil) that could be left where it was. This would make for lower process costs since there is no need to move large quantities of soil material.

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Ultrasound means vibrations which are similar to sound waves, but with frequencies too high to be detected by human ear. All developments within the area of power ultrasound applications lead to the creation of environmentally friendly processes and compounds, emphasizing the role of ultrasound in “green chemistry”. Ultrasound technology is considered not easy to use in industrial processes, since devices providing high sonic energy are not easy to construct. This thesis investigated on a semi-pilot scale if it is possible to enhance the disintegration of three quite different samples: polymers, sludge, and contaminated soil by using ultrasound.

The thesis indicated that it is possible to enhance the disintegration of polymers by means of ultrasonic power only when the cavitation threshold was exceeded. Above the cavitation threshold, the most extensive degradation took place at the lowest ultrasonic frequency used. The thesis showed that the extent of ultrasonic depolymerization decreased with decreasing molecular mass. Also it was found that ultrasonic irradiation caused narrowing of the molecular mass distribution. In the cases where the initial dynamic viscosities of polymer solutions were not the same the higher was the initial dynamic viscosity the faster was the degradation. Ultrasonic disintegration of sludge increased the soluble chemical oxygen demand and therefore the production of methane in anaerobic digestion. Multivariate data analysis suggested that ultrasonic power, sludge dry solids, sludge temperature, and ultrasonic treatment time significantly affected the sludge disintegration. It was also found that high ultrasound power together with a short treatment time was more efficient than low ultrasound power with a long treatment time. Ultrasound improved the soil remediation results in heavy medium separation. This phenomenom was based on the fact that the amount of ultrafine metal fraction was diminished when attrition conditioning was replaced by ultrasound. The remediation process produced cleaned soil that could be left where it was. This would reduce process costs and avoid the need to transport large amounts of soil material.

In this thesis it was shown that it is possible to use ultrasound on a semi-pilot scale to enhance the disintegration of three quite different samples: polymers, sludge, and contaminated soil.

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