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**Utilization of Pressurized Hot Water and Supercritical Water
in the Treatment of Polluted Water and Soil**

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Academic Dissertation

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PREFACE

This thesis is based on research carried out in the Laboratory of Analytical Chemistry of the Department of Chemistry, University of Helsinki, during the years 1996-2002.

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ABSTRACT

The changes that occur in the physico-chemical properties of water at high temperatures and pressures were exploited in the treatment of polluted water and soil. Pressurized hot water oxidation (PHWO) and supercritical water oxidation (SCWO) were applied in the oxidation of aqueous solutions of phenolic compounds. In addition to hydrogen peroxide, potassium persulphate was applied as oxidant. Furthermore, a relatively new technique utilizing pressurized hot water for extraction of organic compounds (PHWE) from solid samples was coupled on-line to SCWO to extract PAHs from sea sand and soil and to destroy the compounds under supercritical conditions with hydrogen peroxide as oxidant.

Continuous flow equipment for PHWO/SCWO and PHWE-SCWO was constructed in the laboratory. In view of the corrosiveness of water at elevated temperatures and pressures, Inconel 600 was chosen as the material inside the heated reaction tube. The main tool for the analysis of the effluent was a gas chromatograph-mass spectrometer system (GC-MS); also a total organic carbon (TOC) analyser and an atomic absorption spectrophotometer (AAS) were employed.

In PHWO/SCWO, phenol, 2,3-dichlorophenol, *m*-cresol and 4-chloro-3-methylphenol were oxidized under various conditions. Temperature and reaction time had a major effect on the oxidation efficiency. With potassium persulphate as oxidant, conversions of the organics close to 100% were achieved at temperatures of ca. 150°C and in reaction times of ca. 30 s. With hydrogen peroxide, the temperatures needed for similar conversions were considerably higher. Over 90% removal of TOC was obtained with both oxidants, but the temperatures required were lower with potassium persulphate. Preheating of the potassium persulphate or hydrogen peroxide solution before entering the reaction tube had a negative effect on the conversions owing to the decomposition of the oxidant. Though potassium persulphate worked effectively at relatively low temperatures, the sulphate that is released would need to be removed in wastewater treatment. Additionally, nickel and chromium concentrations of the effluent (corrosion) were more abundant with potassium persulphate than with hydrogen peroxide as oxidant.

Oxidation of 4-chloro-3-methylphenol was also studied in gas phase, with hydrogen peroxide as oxidant. Excellent conversions were achieved in very short reaction times, but the major reaction products, 4-chlorophenol, 3-methylphenol and phenol were more abundant in gas than in liquid phase. Higher concentrations of these products were found with preheated than with non-preheated hydrogen peroxide solution.

PHWE-SCWO was applied in the treatment of spiked sea sand (toluene or dichloromethane as solvent for PAHs) and real environmental soil. Extraction efficiency

was dependent on temperature and extraction time. With the spiked sand, a temperature of 300°C and extraction time of ca. 20 min were required for ca. 70-80% recoveries of PAHs of low and medium molecular mass. Recoveries were lowest for high molecular mass perylene. With the real soil sample, the amounts of organics extracted were compared with those obtained by Soxhlet extraction and ASE. In general, recoveries of PAHs were better with PHWE (T = 300°C, time = 20 min) than with the other methods. In particular, the amounts of highly volatile naphthalene and acenaphthylene extracted were significantly better with PHWE. In addition to the extraction efficiency, short extraction time and lack of need for organic solvent were advantages of PHWE over Soxhlet extraction.

Hydrogen peroxide concentration, temperature and reaction time were the major parameters tested in optimisation of the oxidation conditions in PHWE-SCWO. The best conversions were achieved at the maximum instrument temperature of 425°C. With spiked samples (toluene as solvent for PAHs), conversions >97% were obtained for PAHs and toluene at 425°C with oxidant concentration of 112.6 g/l. The most abundant reaction products formed in the oxidation of toluene were benzaldehyde and benzoic acid. The conversions of PAHs with spiked samples were higher with dichloromethane than with toluene as solvent. Conversions were also excellent with the real soil sample, and the reduction in TOC concentration was at best ca. 91%. Most probably, higher temperatures and/or longer reaction times would be needed for higher TOC removal. The oxidation of PAHs in supercritical water was non-selective; no significant difference was observed in the oxidation efficiencies of the individual PAHs.

LIST OF ORIGINAL PAPERS

The dissertation is based on the following five publications and manuscripts, hereafter referred to by their roman numerals (I-V).

I. J. Kronholm, P. Jyske and M.-L. Riekkola, Oxidation Efficiencies of Potassium Persulfate and Hydrogen Peroxide in Pressurized Hot Water with and without Preheating. Reproduced with permission from *Ind. Eng. Chem. Res.* 39 (2000) 2207-2213. Copyright 2000 American Chemical Society.

II. J. Kronholm, S. Huhtala, H. Haario and M.-L. Riekkola, Oxidation of 4-Chloro-3-methylphenol in Pressurized Hot Water in Liquid and Vapor Phases. Reproduced with permission from *Adv. Env. Res.* (in press). Copyright 2002 Elsevier Science.

III. J. Kronholm, H. Metsälä, K. Hartonen and M.-L. Riekkola, Oxidation of 4-Chloro-3-methylphenol in Pressurized Hot Water/Supercritical Water with Potassium Persulfate as Oxidant. Reproduced with permission from *Env. Sci. Technol.* 35 (2001) 3247-3251. Copyright 2001 American Chemical Society.

IV. J. Kronholm, T. Kuosmanen, K. Hartonen and M.-L. Riekkola, Destruction of PAHs from Soil by Using Pressurized Hot Water Extraction Coupled with Supercritical Water Oxidation. Reproduced with permission from *Waste Manage.* (accepted for publication). Copyright 2002 Elsevier Science.

V. J. Kronholm, J. Kalpala, K. Hartonen and M.-L. Riekkola, Pressurized Hot Water Extraction Coupled with Supercritical Water Oxidation in Remediation of Sand and Soil Containing PAHs. Reproduced with permission from *J. Supercrit. Fluids* (in press). Copyright 2002 Elsevier Science.

ABBREVIATIONS

AAS	atomic absorption spectroscopy
AC	activated carbon
AOP	advanced oxidation process
ASE	accelerated solvent extraction
C _p	critical point
CSTR	continuous stirred tank reactor
GC	gas chromatography
DPTMDS	diphenyltetramethyldisilazane
IC	inorganic carbon
i.d.	inner diameter
ISTD	internal standard
IUPAC	International Union of Pure and Applied Chemistry
LC	liquid chromatography
LLE	liquid-liquid extraction
MS	mass spectrometry
n.a.	not analysed
ND	not detected
o.d.	outer diameter
ODS	octadecylsilane
PAH	polyaromatic hydrocarbon
PCB	polychlorinated biphenyl
PFR	plug flow reactor
PHW	pressurized hot water
PHWE	pressurized hot water extraction
PHWO	pressurized hot water oxidation
PLE	pressurized liquid extraction
RSD	relative standard deviation
SC	supercritical
SCF	supercritical fluid
SCW	supercritical water
SCWO	supercritical water oxidation
SFC	supercritical fluid chromatography
SFE	supercritical fluid extraction
SPME	solid phase microextraction
STP	standard temperature and pressure
T _p	triple point
TC	total carbon
TIC	total ion chromatogram

TOC	total organic carbon
UV	ultraviolet (light)
WAO	wet air oxidation
WO	wet oxidation

SYMBOLS

d	density (kg m^{-3})
d_c	critical density (kg m^{-3})
d_r	reduced density
D	diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
E_A	activation energy (J mol^{-1})
H	enthalpy (J)
k	reaction rate constant ($\text{m}^3 \text{mol}^{-1})^{n-1} \text{s}^{-1}$)
K_w	dissociation constant of water
M	molecular mass (kg mol^{-1})
P	pressure (bar, 1 bar = 100,000 Pa)
P_c	critical pressure (bar)
P_r	reduced pressure
R	gas constant (= $8.314 \text{ J K}^{-1} \text{mol}^{-1}$)
T	temperature ($^{\circ}\text{C}$, $0^{\circ}\text{C} = 273.15 \text{ K}$)
T_c	critical temperature ($^{\circ}\text{C}$)
T_r	reduced temperature
α	polarisability ($\text{C}^2 \text{m}^2 \text{J}^{-1}$)
γ	surface tension (N m^{-1})
ΔH_v	heat of vaporisation ($\text{J kg}^{-1} \text{mol}^{-1}$)
ΔV^{\ddagger}	activation volume ($\text{m}^3 \text{mol}^{-1}$)
δ	solubility parameter (hildebrand unit H, 1 H = 1 (cal cm^{-3}) ^{1/2} , 1 cal = 4.19 J)
ϵ_r	relative permittivity (=dielectric constant)
η	viscosity (Pa s)
λ	wavelength (m)
μ	electric dipole moment (C m, 1 debye unit D = $3.33564 \times 10^{-30} \text{ C m}$)
v	volume flow rate ($\text{m}^3 \text{s}^{-1}$)

1. INTRODUCTION

The environment and its pollution are a cause of increasing concern. Hazardous organic compounds originating in human activity are present almost everywhere, and much attention is being paid to their removal and destruction. Various techniques have been developed for the treatment of contaminated soil and water. Finding techniques that at the same time are effective, economic, safe, environmentally friendly and practical is no easy task, however. In laboratory scale, new knowledge and advanced techniques have made it possible to replace traditional analytical methods relying on hazardous organic solvents by alternative approaches that reduce or eliminate the need for organics. In addition to the environmental issues, improving the efficiency and reliability of techniques and reducing the analysis time are of major importance.

Various biological, chemical and physical techniques, and their combinations, have been applied to the treatment of wastewater, sludge and soil. The technique to be used depends on various factors, not least the nature and concentrations of the pollutants. Many techniques suffer from serious drawbacks. Biological methods, for example, have been widely used, but they tend to be slow and some organics are toxic to microorganisms. Incineration is significantly faster than biological methods, but the operating costs are high and the off-gases must be purified. Activated carbon (AC) is effective in removing contaminants from waste streams, but the AC itself must be regenerated or handled as a hazardous waste.

Pressurized hot water oxidation (PHWO) and supercritical water oxidation (SCWO) have been utilized in the treatment of wastewaters and sludges for a relatively short time. These techniques are based on the altered physico-chemical properties of water at elevated temperatures and pressures. PHWO often requires longer reaction times than SCWO, or use of a catalyst owing to the lower operating temperatures, and some reaction intermediates may remain in the effluent. Choice of oxidant may also affect the efficiency of PHWO/SCWO. The SCWO technique is capable of destroying hazardous organics, normally in some tens of seconds at 400-600°C, but corrosion problems may arise and blockage may occur due to the precipitation of inorganics. Attempts have been made to solve these problems, but the final breakthrough is still to come.

Soxhlet extraction, liquid-solid extraction and sonication have often been applied to environmental samples (soils and sediments) in laboratory-scale. These techniques, relying on organic solvents, may nowadays be replaced with techniques using reduced volumes of solvents or even no solvent. For example, solid-phase microextraction (SPME), supercritical fluid extraction (SFE, carbon dioxide often as fluid) and accelerated solvent extraction (ASE) have been successfully applied. Pressurized hot

water extraction (PHWE) is a relatively new technique. Like SCWO and PHWO, it utilizes the changed physico-chemical properties of water at elevated temperatures and pressures. With PHWE, good recoveries for organics can often be achieved in 20 min at 300°C, and the selectivity to compounds of different polarity can be adjusted through changes in temperature and pressure.

In this study, aqueous solutions of four model pollutants – phenol, 2,3-dichlorophenol, *m*-cresol and 4-chloro-3-methylphenol – were treated by PHWO or SCWO in continuous flow equipment constructed in the laboratory (I-III). Phenols are hazardous compounds, often present in industrial wastewaters. Hydrogen peroxide and potassium persulphate were employed as oxidants, under various conditions. Potassium persulphate has been used in several oxidation processes in batch mode, but there was sparingly information about its use in continuous flow systems. For both oxidants, the main parameters in optimizing the conditions were temperature and reaction time. Studies were also made in gas phase with hydrogen peroxide as oxidant. The effect on the oxidation efficiency of preheating the capillaries delivering aqueous streams of oxidant and organics was tested with both oxidants. In interpreting the suitability of the oxidant, study was made of conversion of the organics, reaction products (intermediates), total organic carbon (TOC) concentration of the effluent and corrosion (nickel and chromium concentrations of the effluent). Experiments were also carried out under various conditions to determine the amount of sulphate released to the effluent when potassium persulphate was used as oxidant.

On-line coupled PHWE-SCWO equipment was constructed in the laboratory to extract organics (mainly PAHs) from solid samples and to oxidize them directly, under supercritical conditions, with hydrogen peroxide as oxidant (IV, V). No PHWE-SCWO equipment is commercially available today. PHWE-SCWO can be considered an environmentally friendly remediation technique for polluted soil with on-line destruction of the extractants; no organic solvent is needed in the process. PAHs (often formed during incomplete combustion) were chosen as the pollutants because they are widespread in the environment and some of them are carcinogenic and/or mutagenic. Experiments were begun with spiked sea sand samples, and later real contaminated soil was treated. In the PHWE step, the effects of temperature and extraction time on the recovery of PAHs of different molecular mass (selectivity) were studied. In the analysis of real soil samples, the extracted amounts of PAHs were compared with those obtained with Soxhlet extraction and ASE. In PHWE-SCWO of PAHs, the effects of oxidant concentration, reaction time and temperature on the oxidation efficiency were studied by examination of conversions of the PAHs, reaction products and the TOC concentration of the effluent.

2. OBJECTIVES OF THE STUDY

The overall aim of this work was to develop continuous flow equipment capable of efficient, reliable and safe destruction of organic pollutants in water and soil at high temperatures and pressures. Water is a cheap and readily available “green” solvent and reaction medium. The feasibility of supercritical water oxidation and pressurized hot water oxidation was investigated for the treatment of aqueous phenolic solutions, and the usefulness of potassium persulphate as oxidant was tested under various conditions. For comparison, hydrogen peroxide was applied as oxidant. Pressurized hot water extraction was coupled on-line to SCWO for the treatment of contaminated solid samples. In these studies, the main emphasis was on the investigation of destruction of PAH compounds.

The more specific targets of the research were

- to construct safe, simple, reliable and efficient laboratory-scale equipment for continuous flow PHWO and SCWO treatment of aqueous solutions (I-III),
- to evaluate the suitability of potassium persulphate as an oxidant alternative to hydrogen peroxide over a wide range of temperatures (I, III),
- to study factors affecting the oxidation efficiencies of phenol, 2,3-dichlorophenol, *m*-cresol and 4-chloro-3-methylphenol (I-III),
- to study the effects of preheating of the oxidant on the oxidation efficiency (I, II),
- to compare gas with liquid and supercritical states as oxidation medium (II),
- to clarify the effects of oxidation conditions on corrosion, *i.e.* nickel and chromium concentrations of the effluent (I-III),
- to construct laboratory-scale equipment for safe, simple, reliable and efficient PHWE-SCWO treatment of solid samples (IV, V),
- to apply PHWE-SCWO to spiked sea sand and real contaminated soil (IV, V),
- to study parameters affecting the extraction and oxidation efficiencies of aromatics, mainly PAHs (IV, V),
- to compare the efficiencies of extraction of PAHs obtained by PHWE, Soxhlet extraction and ASE (V).

For the first time in this work, potassium persulphate was used as oxidant in continuous flow equipment where supercritical water and pressurized hot water were used as oxidation medium. Likewise, for the first time, study was made of the effect of preheating of persulphate on the oxidation efficiency of phenolic compounds. Unique on-line coupled PHWE-SCWO equipment was constructed and applied. In addition, new information about the extraction and oxidation of PAHs was obtained.

3. SUPERCRITICAL FLUIDS

Denys Papin demonstrated the effect of pressure on the boiling point of water as early as 1680 [1]. It was not until 1822, however, that Baron Cagniard de LaTour discovered the supercritical state [2]. He defined supercritical fluid as fluid that exhibits characteristic properties of both liquid and gas. Other researchers continued his work, and the nature of the supercritical state and the significance of the critical point were debated, among others, by Michael Faraday [3] and Thomas Andrews [4, 5]. It was Andrews who introduced the term “critical point”. Hannay and Hogarth undertook the first systematic studies on solubility in SCFs in 1879-1880 [6, 7]. Today, a huge number of publications have accumulated in this area of research, and the interest in supercritical fluids as alternative solvents and reaction media continues to grow.

IUPAC defines SCF as any element, substance or mixture that is heated above its critical temperature T_c and pressurized above its critical pressure P_c (see Fig. 1) [8]. The point corresponding to the values of T_c and P_c is called the critical point, above which the substance cannot be liquefied with rise in pressure or vaporized with increase in temperature. As such, SCF exists as a single phase. In addition, pressure must be below the pressure required to solidify SCF, because the solid phase can exist above the critical point at very high pressures. For example, the pressure needed to solidify CO_2 at its critical temperature is 5700 bar [9] and that for water is 140,000 bar [10]. Fluid density at the critical point is called the critical density (d_c).

The terms reduced pressure (P_r) and reduced temperature (T_r) are often used. A reduced value is defined as the ratio of the actual absolute value to the critical point value. If P_r and $T_r > 1$ the substance is in the supercritical state. The “law of corresponding states” implies that compounds behave similarly under the same values of the reduced variables [11]. The terms “subcritical” and “near critical” are often used for the state below the critical point. Neither term is precisely defined, however. Accordingly, the term “pressurized hot substance” and, with water, the term “pressurized hot water” are used in this thesis.

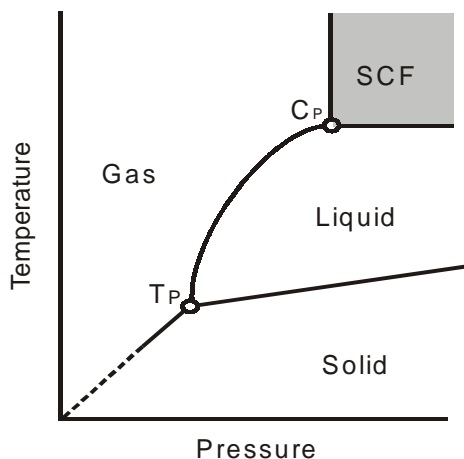


Figure 1. Phase diagram for a pure substance; region of supercritical fluid (SCF) shadowed.

3.1. Properties of supercritical fluids

A supercritical fluid possesses the properties of both liquid and vapour and is often described as an intermediate between liquid and vapour. In the vicinity of the critical point, density is a strong function of pressure. The densities of SCFs resemble those of liquids [12-15]. The dissolving power of SCF is high, and solubility can be adjusted through changes in temperature and pressure [16-19]. The solubility of a compound increases with the density of SCF. Polar solvents, like ammonia and water, exhibit greater change in their dissolving power with increase in density than do less polar solvents. The effect of temperature on solubility is not always straightforward. With increase in temperature, two competing effects come into play: first, the vapour pressure of a solute increases and with it the solubility; second, the density and solvent power of the fluid decrease and with it the solubility. This temperature effect is commonly described as retrograde vaporisation, and it is at its strongest in the vicinity of the critical point. At constant density, increasing the temperature enhances the solubility of a compound.

The solubility of a compound in SCF is of major interest in numerous applications. In addition to temperature and density, the solubility is affected by the chemical properties of both the fluid and the solutes. Information about the solubility of a compound can be achieved with the Hildebrand solubility parameter δ [20, 21]:

$$\delta = \sqrt{\frac{d(\Delta H_v - RT)}{M}} \quad (1)$$

where d is the density and ΔH_v the heat of vaporisation. The solubility parameter is a measure of intermolecular forces in pure substances. According to Hildebrand, the heat of mixing ΔH can be defined as follows:

$$\Delta H = v_1 v_2 (\delta_1 - \delta_2)^2 \quad (2)$$

where v_1 and v_2 are the partial volumes of the solvent and solute, respectively, and δ_1 and δ_2 are the solubility parameters of the solvent and solute, respectively. As a rule, solvent are readily miscible if the difference in their solubility parameters $\Delta\delta$ is $\leq 4-6$ units. However, solvents with similar solubility parameters do not always have similar solvation properties because of dissimilar dipole moments and polarizabilities. Giddings *et al.* [22] have modified the theory for the needs of SCFs where the solubility parameter of the fluid is given by

$$\delta_1 = 1.25 \sqrt{P_c} \frac{d_r}{d_{r \text{ liq}}} \quad (3)$$

where P_c is the critical pressure, d_r reduced density of the supercritical fluid, and $d_{r \text{ liq}}$ that of the fluid in the liquid state.

The dielectric constant (ϵ_r) is a good measure of solvent-solute interactions and it can be related to polarity: a high dielectric constant favours the solubility of high polarity compounds and a low dielectric constant the solubility of low polarity compounds. In the supercritical region, the dielectric constant is a function of pressure. For example, ϵ of carbon dioxide is increased only slightly but that of water by several magnitudes with pressure in the compressible region [23, 24].

The higher the diffusion coefficient (D) of a solute in a fluid, the faster is the mass transfer. Supercritical fluids are ideal media for mass transfer because diffusion coefficients of solutes are higher in SCFs than in liquids [25-28]. In SCFs, diffusivity decreases with increase in pressure and increases with temperature, especially in the vicinity of the critical point. Viscosity (η) of SCFs lies between that of liquids and gases, which also enables more favourable mass-transfer properties than in liquids. Viscosity is a property of a fluid to resist change of form, *i.e.* it is a sort of internal friction. At a given constant temperature, viscosity increases with pressure [29, 30].

Surface tension (γ) can be determined by the attraction of molecules at the surface of a liquid into the body of the liquid because the attraction of the underlying molecules is greater than the attraction of the vapour molecules on the other side of the surface [31]. Surface tension of SCFs is zero. Figure 2 presents the relationships between the basic properties of a SCF.

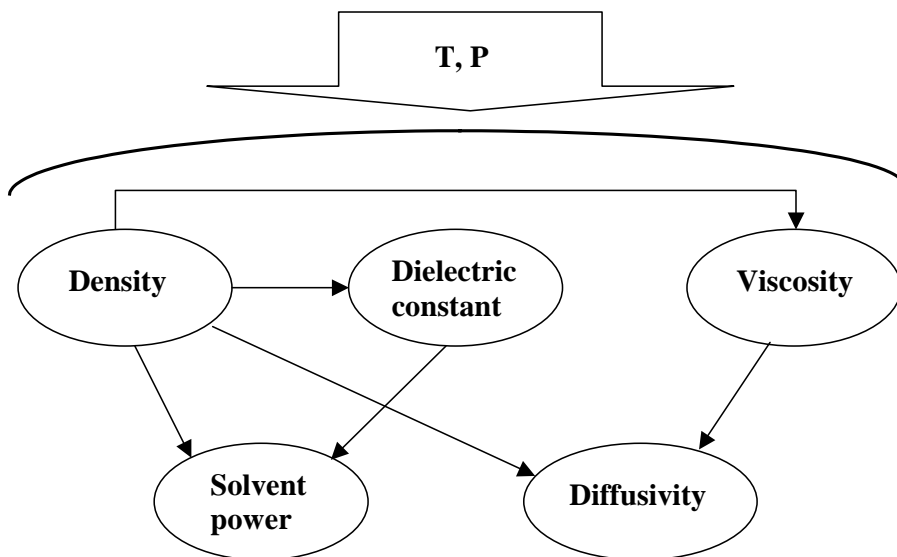


Figure 2. Basic properties of a SCF and their relationships.

3.2. Some common supercritical fluids

Properties of some pure substances commonly used as SCFs are listed in Table 1 [21, 32, 33]. The environmental and health benefits of SCFs are often considered of prime importance. For example, supercritical fluids can be used in place of hazardous organic solvents. Also, economic and technical issues are of interest. Carbon dioxide is the most common SCF today. It is non-toxic, relatively cheap and non-flammable. These properties together with the low critical temperature and pressure make it the SCF of choice in many applications, for example in SFE, SFC, other separation processes and various reactions [34-40]. However, carbon dioxide is non-polar, which means that its solvent properties are limited. To overcome this shortcoming, it often is necessary to add a polar modifier, such as methanol.

Another widely used and environmentally friendly supercritical fluid is water, which will be discussed in detail in Section 3.3. Many other substances possess excellent SCF properties, but they may be hazardous in use. For example, organics may react vigorously with SC N₂O (strong oxidant) and explosions have resulted [41, 42]. Sometimes the useful properties of SCFs can be achieved to some extent at lower temperatures than the critical values.

Table 1. Some pure substances and their critical temperature and pressure, molecular mass, relative permittivity, electric dipole moment and solubility factor. Data collected from references 21, 32 and 33.

Compound	T _c (°C)	P _c (bar)	M	ε _r ^a	μ (Debye)	δ ^b (H)
Ammonia	132.4	113.2	17.03	16.9 ²⁵	1.47	16.3
Argon	-122.5	48.6	39.95	1.5 ⁻¹⁹¹	0	5.3
Carbon dioxide	31.1	73.8	44.01	1.6 ²⁰	0	6.0
Dichloromethane	237.0	60.8	84.93	9.1 ²⁰	1.60	9.8
Ethanol	243.0	63.8	46.07	24.3 ²⁵	1.69	10.0
Hydrogen chloride	51.5	82.6	36.46	4.6 ²⁸	1.08	-
Methanol	239.5	80.8	32.04	32.6 ²⁵	1.70	14.5
n-Hexane	234.5	30.3	86.18	1.89 ²⁰	-	7.3
Nitrous oxide	36.4	72.5	44.01	1.61 ⁰	0.17	-
n-Pentane	196.6	33.7	72.15	1.8 ²⁰	-	7.0
Sulphur hexafluoride	45.5	37.6	146.1	1.8 ⁻⁵⁰	0	-
Water	374.1	220.6	18.02	78.5 ²⁵	1.85	9.4

^a Temperature (°C) shown as a superscript

^b Solubility parameter for liquid at 25°C expressed as (cal cm⁻³)^{1/2}, *i.e.* in hildebrand units (H)

3.3. Supercritical water and pressurized hot water

Supercritical water (SCW) has existed for a very long time in the Earth's crust. The critical temperature and pressure of water are high (T_c=374°C, P_c =221 bar), however, and the existence of this state was not demonstrated until the 1800s. Cagniard de LaTour noted in 1822 that water at temperatures a little below the critical temperature is particularly reactive [2], and Gabriel-Auguste Daubrée carried out pioneering experiments above the critical temperature of water in the middle of the 19th century [43]. Charles Friedel, better known for the Friedel-Crafts reaction, also did early studies on hydrothermal reactions [44, 45]. Today, water at elevated temperatures and pressures and its applications are investigated widely.

SCW exhibits properties also characteristic of other SCFs; these include high solvating power, compressibility and favourable mass transport ability (Section 3.1.). In general, organic compounds and gases are soluble in SCW, while inorganic compounds such as salts are insoluble.

PHW is used at temperatures above 100°C but below 374.1°C. In PHW applications, pressure is usually high enough to keep the water in liquid state. The term PHW may also be applied to the vapour phase, where sufficient pressure is usually applied to provide transportation. PHW can be used in applications where moderate temperatures are sufficient to obtain selected physico-chemical properties. For example, mass transport properties and solvent-solute interactions in PHW (T = 200-300°C) are often suitable for extractions. Table 2 summarizes some advantages and disadvantages of SCW and PHW, especially for the needs of PHWO and SCWO and PHWE.

Table 2. Advantages and disadvantages of SCW and PHW for PHWO and SCWO and PHWE.

Advantages	Disadvantages
SCW is a good solvent for all kinds of organics (can replace organic solvents)	High critical temperature and pressure make demands on energy and materials
PHW and SCW are excellent reaction media	High reactivity may cause problems in PHWE (<i>e.g.</i> decomposition and unwanted side-products)
Good selectivity is provided as a function of temperature, especially in the vicinity of the critical point	Corrosion problems arise, especially with some oxidant added; materials used in equipment must resist corrosion (expensive)
Water is environmentally friendly, non-toxic, non-flammable and cheap	Blockage of the equipment is possible in SCW because inorganics precipitate
Water (pure enough) is readily available	Extracts in PHWE are dirty because water dissolves almost everything
Water often acts as an autocatalyst	High temperature and pressure of SCW liable to create dangerous working conditions, especially at large scale

3.4. Dissolution and solvent properties of water

A good rule of thumb is that “like dissolves like”, *i.e.* chemically similar compounds are soluble in each other. When a solute is dissolved in a solvent, the solvent molecules penetrate between the solute molecules and form a layer around them. The process, in which new forces are formed between the solute and solvent molecules and the attractive forces between solute molecules are destroyed, is called solvation [46]. The solubility parameter (δ), dipole moment (μ), polarisability (α), hydrogen bonding and molecular sizes of the solvent and solute all have an effect on the solvation process. If the solutes

are not soluble in the solvent, energy is required to overcome the difference in the attractive forces.

In contrast to other solvents, water and aqueous solutions have special properties that are strongly sensitive to temperature and pressure. With water as solvent, ionic, hydrogen bonding, dipole-dipole, induction and dispersion forces are of importance.

Ionic (Coulomb) forces are important when ionic compounds are dissolved in polar solvent. The force depends on the electrical charges of the ions and the distance between them. The force of attraction between the ions is inversely proportional to the dielectric constant ϵ of the solvent, and is reduced as new ion-dipole forces are formed. The dielectric constant must be considered as a bulk property and not the property of one molecule alone. At room temperature, water is a polar solvent with some special properties different from many other substances: the dielectric constant of water (ϵ_r ~78.5) is quite high, and it favours the solubility of ionic and polar compounds. However, under supercritical conditions, ϵ_r can be decreased close to 1 favouring the solubility of less polar organic compounds [47-51]. This trend can be seen in Fig. 3.

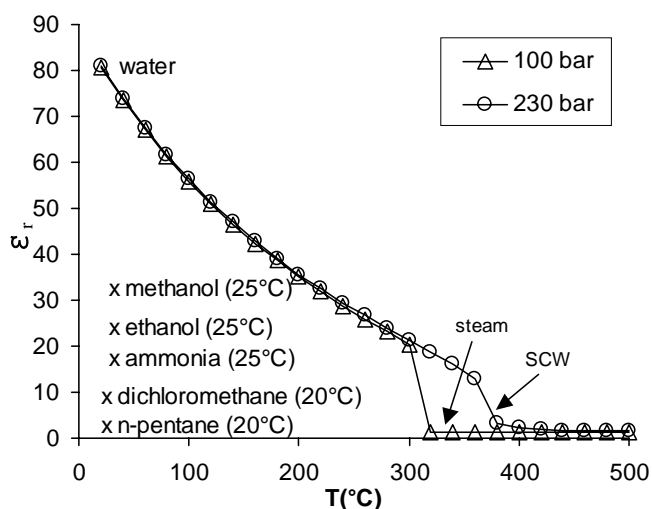


Figure 3. Relative permittivity of water as a function of temperature and of some common organic solvents at 20 or 25°C.

Water molecules can act as both hydrogen donors and hydrogen acceptors, and thus are able to form hydrogen bonds with one another. Hydrogen bonds are dependent on the mutual orientation of the molecules, and temperature affects the orientation strongly. At STP, hydrogen bonding of water is strong. Under supercritical conditions, hydrogen bonding is weakened significantly [52-58].

Dipole-dipole forces are attractive forces between polar molecules with permanent dipole moments. The forces between the dipoles weaken dramatically with increase of temperature. Induction forces are generated when non-polar compounds are dissolved in polar solvent. The electric field of a molecular dipole leads to charge displacement in the neighbouring molecule and thus to induction of a dipole. Dispersion (London – Van der Waals) forces are present in all atoms and molecules. These are generated by mutual induction of atomic dipoles due to electromagnetic field between the nucleus and electrons of the atom. Induction and dispersion forces are only weakly dependent on temperature.

The ion product, or dissociation constant (K_w), for water is about three orders of magnitude higher in the vicinity of the critical point of water than it is at STP. Consequently, higher H^+ and OH^- ion concentrations can be achieved there than at STP. Near the critical point, the dissociation of water itself generates high H^+ ion concentration and some acid-catalysed reactions may occur without any acid added. However, when the critical point is exceeded, K_w decreases rapidly. For example, K_w is about nine orders of magnitude lower at 600°C and 250 atm than it is at STP.

3.5. Reactions in water at elevated temperatures and pressures

Normally most organic reactions do not occur, or they take place slowly, in water at STP. The high solvating power, compressibility and favourable mass transport properties of SCW make it an interesting medium for reactions. SCW allows manipulation of the reaction environment through adjustment of pressure and temperature. In this way, for example, the solubilities of the reactants can be enhanced and the interphase transport limitations on reaction rates eliminated.

Pressure has a theoretical influence on the rate and/or selectivity of reactions, because the properties of PHW and SCW can be altered through the manipulation of pressure. The standard thermodynamic relationship demonstrates this sensitivity to pressure [37, 59]:

$$\left[\frac{\partial \ln k}{\partial P} \right]_T = -\frac{\Delta V^\ddagger}{RT} \quad (4)$$

where k represents the reaction rate constant and ΔV^\ddagger the activation volume (the volume change undergone by the reactants on reaching the transition state). Pressure changes in the vicinity of the critical point may result in considerable variations in k . The effect of pressure on k is related to its effect on the density of SCW as well as on its diffusivity, viscosity, dielectric constant and dissolving power. The rate constant is increased with the density of water. Because the overall rate of a reaction is a product of the rate constant

and the concentration of the reactant in SCW, also the polarity of SCW must be taken into account to guarantee maximum solubility of a reactant in the fluid.

Local properties in the vicinity of a solute molecule dissolved in a SCF are very different from the average bulk solution properties [60-62]. Because of attractive inter-molecular forces, supercritical solvent molecules cluster around the solute molecules resulting in increased local density relative to the average bulk density. Clustering may have effect on the reactions in SCF because it may alter the reaction mechanism by lowering its activation energy E_A . The high compressibility of supercritical water favours the formation of solute-solvent clusters and thus water may act as a catalyst. Occasionally, the reactivity of SCW is a limiting factor in some applications, for example, in SFE.

4. OXIDATION IN WATER AT ELEVATED TEMPERATURES AND PRESSURES

Supercritical water oxidation and pressurized hot water oxidation are advantageous techniques utilizing the changed physico-chemical properties of water at elevated temperatures and pressures. SCWO can be considered as an extension of PHWO, which operates below the critical temperature (and pressure). Figure 4 shows that the number of articles in the area of SCWO and PHWO has increased dramatically over the past thirty years. The apparent decline in the number of articles published in 2001 probably only reflects the incompleteness of the search result.

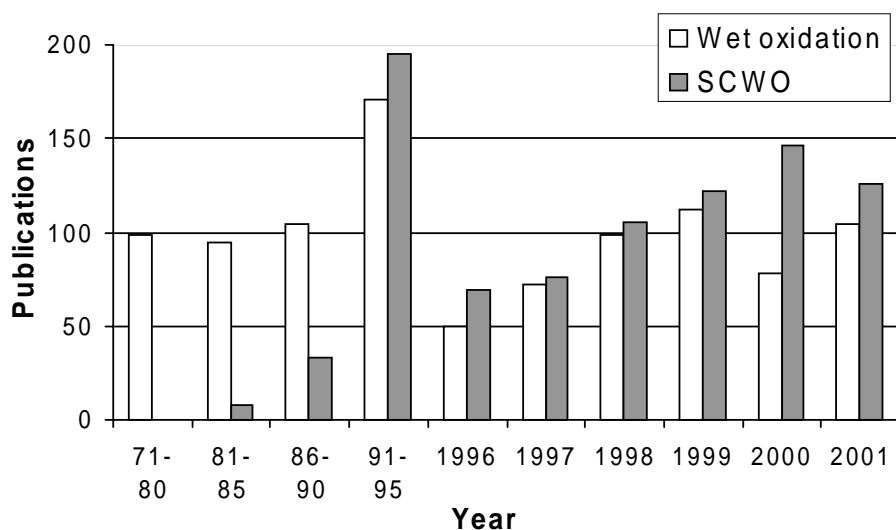


Figure 4. Number of articles on PHWO and SCWO listed in Chemical Abstracts 1971-2001. “Wet oxidation” and “SCWO” were used as key words in the search process.

4.1. Supercritical water oxidation

Supercritical water oxidation is a form of hydrothermal treatment. Several review-type papers give a good overview of the technique [37, 63-69]. A homogeneous, single phase results when organic compounds and oxidant are dissolved in supercritical water. The oxidation process proceeds without interfacial mass transfer limitations and the solutes have high diffusivity, facilitating the oxidation process. In addition to a solvent, SCW can also act as a major reactant affecting the rate of organic destruction. The application of SCWO to wastewater treatment was introduced in the middle of the 1980s. The first patent in the field was that of Dickinson published in 1981 [70]. A short time later, Michael Modell founded MODAR Inc. in Massachusetts in USA as a commercial venture to develop and market SCWO technology. The first commercial SCWO facility in the world for treating industrial wastewater became operational in 1994. Numerous studies have now confirmed that SCWO is an effective technique in wastewater treatment.

SCWO is economically attractive for the treatment of wastewaters that contain organic compounds in concentrations of 1-20 w-% [71]. With this strength of solution and properly designed heat exchangers, the heat developed by the oxidation will maintain the required reaction temperature. With lower concentrations of organics, the autothermal process does not work, and auxiliary fuel is required. On the other hand, if the concentration of the organics exceeds 20-25%, incineration becomes competitive. Typical operational temperatures in SCWO are 400-650°C and pressures ca. 250 bar. Catalysts can be applied to lower the activation energy required [72, 73]. It is of primary importance that the catalyst is physically and chemically stable, mechanically strong, efficient (exhibits high oxidation rates and complete oxidation) and non-selective. Transition metal oxides (*e.g.* oxides of V, Cr, Mn, Fe, Co, Ni and Cu) and noble metals (*e.g.* Ru, Pt and Pd) are used in catalytic SCWO.

Typically, the main reaction products in SCWO are carbon dioxide and water. Organic heteroatoms are usually converted to acids, salts, oxides or other inorganic compounds. Heavy metals may form oxides or carbonates. Phosphorus is converted to phosphates, sulphur to sulphates and halogens to haloacids (*e.g.* chlorine to hydrogen chloride). Nitrogen-containing compounds are usually converted to N₂ and N₂O. NO_x emissions are not a problem because of the relatively low reaction temperature. Depending on the reaction conditions and reactants, salts may remain dissolved or may condense as a brine solution or precipitate as solid particulates. Inert solids are largely unaffected by the supercritical reaction medium and remain as solids.

Reactions proceed via several intermediates, which should not be present in the final effluent; the parameters affecting the oxidation (*e.g.* temperature and reaction time) should be optimized to avoid this. Three common rate-controlling intermediates are acetic acid, methanol, and ammonia. Formation of the final products as well as the formation and destruction rates of the intermediates affect the global oxidation rate. Oxidation kinetics of acetic acid, methanol and ammonia have been investigated widely [74-79].

Different classes of organic compounds, including alkanes [80], phenols [81-86], chlorinated hydrocarbons [87-90] and nitrogen-containing compounds [91-94], have been treated by SCWO. The technique has been applied to wastewaters and sludges of various kinds: to municipal sewage sludge [95, 96], pulp mill sludge [97, 98], process wastewaters [94], pharmaceutical and biopharmaceutical waste [99] and sludges from water treatment plants [100].

Phenol and substituted phenols have attracted considerable attention, because they are often harmful and toxic and are often present in the wastewaters of diverse industries. Phenol is a common and relatively stable intermediate formed in the oxidation of substituted phenols, and it is often considered a good worst-case model compound. A variety of other intermediates, for example, dimers (*e.g.* biphenols, phenoxyphenols, dibenzodioxins, dibenzofurans, dibenzofuranols), single-ring compounds (*e.g.* hydroquinones) and ring-opening products (*e.g.* acetic acid, maleic acid, formic acid, other organic acids) have been found in the oxidation of phenolics [81-83, 101-103]. The oxidation rates for substituted phenols strongly depend on the identity and location of the substituent; the reactivity of a given substituent is in the order ortho > para > meta.

Some clear trends have been demonstrated in the oxidation kinetics [65, 89, 101, 104, 105]. First, with the oxidant present in large excess of the stoichiometric demand, the oxidation rate is in most cases independent of or only weakly dependent on the oxidant concentration. Second, pseudo-first-order kinetics with respect to the concentration of the starting compounds often applies. Third, the activation energy range, depending on the compound, is between ~30 and 480 kJ/mol.

One working hypothesis is that the oxidation reaction in SCW follows the free-radical (homolytic) mechanism, which often involves an induction period, the generation of a radical pool and a fast free-radical reaction period. This homogeneous SCWO chemistry is analogous to free-radical gas-phase oxidation chemistry in the same temperature regime. Ionic (heterolytic) reaction mechanisms have also been proposed for the oxidation of organics. The particular reaction pathway may depend on the temperature, concentration of the oxidant, presence of a catalyst and the compounds to be oxidized.

4.2. Pressurized hot water oxidation

Pressurized hot water oxidation is carried out at temperatures (and pressures) below the critical point of water. The term “wet oxidation” (WO) is widely applied, and several articles give an overview of the technique, which normally operates at temperatures ~125-320°C and pressures up to 200 bar [106-110]. With oxygen or air as oxidant, the technique which was developed and patented by Frederick J. Zimmermann (the Zimmermann process), is often described as wet air oxidation (WAO) [111, 112]. In fact, the very first patent for WAO was Strehlenert’s, issued in 1911 for the treatment of sulphite liquor from pulp production [113]. WAO became fairly common in the treatment of wastewaters in the 1960s, and the first commercial applications appeared in 1982. With hydrogen peroxide as oxidant, adapted from the classical Fenton’s reagent, the term “wet peroxide oxidation” (WPO) can be applied. In this work, the term PHWO is used independent of the oxidant.

The PHWO technique is not usually as effective as SCWO in the destruction of organics owing to the lower reaction temperature, which results in lower rate constants. The solute-solvent interactions and mass transfer properties may not be as effective as with SCWO limiting the use of PHWO. Thus, PHWO can be applied, for example, in the preliminary detoxification of wastewater, before biological treatment [114, 115]. The oxidation efficiency of PHWO, like that of SCWO, depends on the structure and concentration of the organics, the waste matrix, reaction temperature, oxidant concentration and reaction time. As in SCWO, the main reaction products are carbon dioxide and water, along with various organic and inorganic compounds.

PHWO has been successfully applied to several types of wastewaters to reduce the content of hazardous compounds [116-119]. Typical end products in the oxidation of phenolic solutions are polymeric material (tars), pyrocatechol, hydroquinone and carboxylic acids. Halogenated aromatics are also quite stable and often are not completely destroyed. The higher the temperature, the higher is the efficiency of the oxidation process, and low-molecular mass compounds such as acetaldehyde, acetone, acetic acid and methanol then dominate as break-down products. These compounds are more volatile than the parent compounds and are distributed between the process off-gas phase and the oxidized liquid phase. Typically, the concentrations in the gas phase are 10-1000 ppm; emissions can be controlled by various techniques, *e.g.* granular-carbon adsorption and fume incineration. Catalysts can be used (as in SCWO) to increase the oxidation efficiency.

Free radical and ionic reactions have been proposed for reaction mechanisms in PHWO. An induction period, typical to free radical reactions, has frequently been observed in

PHWO of phenols. The reaction order with respect to phenol has often been found to be one, but other orders have also been reported [120]. The overall rate of WAO is in practice governed by the main reaction products.

4.3. Equipment used in oxidation processes

The reactor (oxidizer) is one of the major parts of the equipment in oxidation processes. Most SCWO and PHWO experiments are carried out in batch or flow reactors (Fig. 5) [121, 122]. Batch-type reactors are designed to provide data under controlled temperatures, pressures and reaction times. Typically, the reactor is quite simple and used in preparative scale in the laboratory. Flow neither enters or leaves the batch reactor. After the reactor has been loaded with water and model compounds, oxygen is often removed with an inert gas (usually nitrogen). The reactor is heated up to the selected temperature and the oxidant is added at the required pressure. A temperature and pressure control unit is needed to control the process. An agitation system is often included in the reactor. Samples can be taken with special sampling facilities. It is also possible to quench the reaction by rapid cooling, and to take samples only after this.

Flow reactors, which are more common in larger-scale operations, are of two basic types: tubular-flow reactors and continuous stirred-tank reactors (CSTR) (Fig. 5). In the tubular-flow reactor (also known as a plug flow reactor, PFR), reactants are passed along the tube so that there is as little intermixing as possible between the reactants entering the tube and the products leaving at the far end. The residence time in the PFR is the same as the reaction time in a batch type reactor. In the CSTR, agitation is used to disperse the reactants thoroughly in the reaction mixture when they enter the tank. Homogeneous stirred-tank systems are analogous to slurry reactors, in which the ratio of liquid to solid is high [123]. Homogeneous reactions, such as polymerisation, are enhanced in slurry reactors. Catalytic oxidation reactions may be carried out in packed or fixed-bed reactors. In fixed-bed reactors, two fluid phases pass through a stationary bed of catalyst either concurrently upward (bubble column fixed bed) or downward (trickle bed) and the ratio of liquid to solid is low.

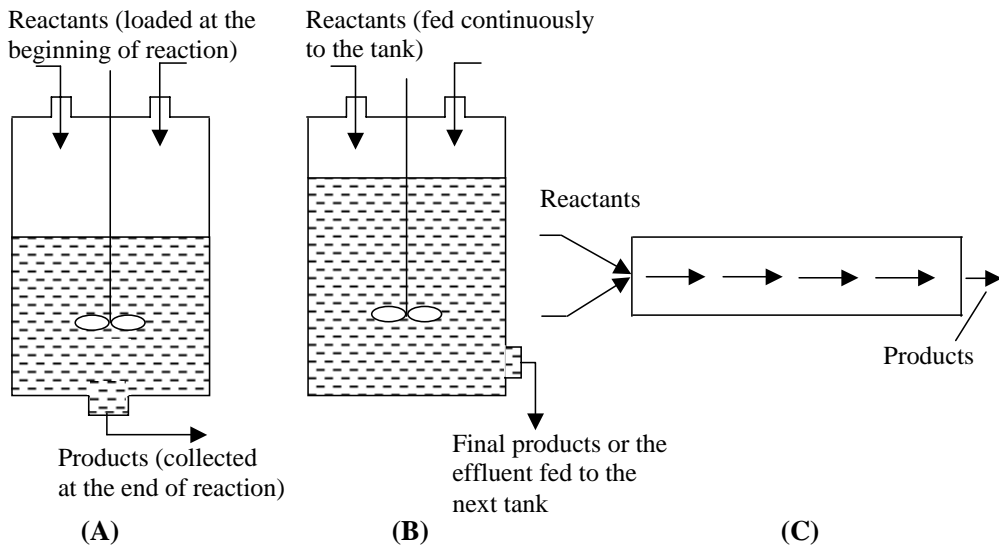


Fig. 5. View of three chemical reactors: A) batch reactor; B) continuous stirred tank reactor (CSTR); C) tubular-flow reactor.

Continuous flow systems tend to be more complicated than batch systems and they require more automation, especially when used in large scale [71, 72, 124]. A simplified construction is presented in Fig. 6. The following parts are often included in SCWO systems: a high-pressure pump for aqueous waste and another pump for oxidant (if in liquid form) or a compressor (where air is used as oxidant), a heating system, preheating tubes, reactor, cooling, a salt separation system and a pressure letdown system.

High-pressure pumps must be capable of pressurizing and feeding aqueous wastewater or slurry to the heated reactor (in heated oven or sand bath, for example). Streams containing large particles or high solids content may require homogenization before treatment. Wastewater and oxidant streams are often preheated with the help of heat exchangers to minimise the need for energy in the reactor.

The exothermic oxidation reaction is initiated when the oxidant and organic waste streams are mixed in the heated reactor. The heat developed will maintain the required reaction temperature if heat exchangers are properly designed and the waste contains only ca. 2% organics [64]. Excess energy can be recovered as steam. A portion of the reactor effluent can be recycled and mixed with the feed streams.

The precipitation of salts is rapid under the almost shock-like conditions. Salts can be separated at the bottom of the reactor as cooled brine or periodically collected as solids. After cooling of the stream leaving the reactor, the liquid-vapour separator may be used to separate the gaseous products of the reaction. The separation is preferably carried out in multiple stages to minimise the erosion of valves and to maximize the separation.

Organics are most often fed to the reactor in aqueous form from a tank. However, they may also be fed to the reactor directly from contaminated soil. For example, Kruse and Schmieder [125] describe SC oxidation in water and carbon dioxide and the construction of on-line equipment with both an SFE (carbon dioxide as fluid) and an oxidation step. Misch *et al.* [126] have applied PHW and SCW to extract organics from contaminated soil and to oxidize them directly with oxygen produced by means of electrolysis.

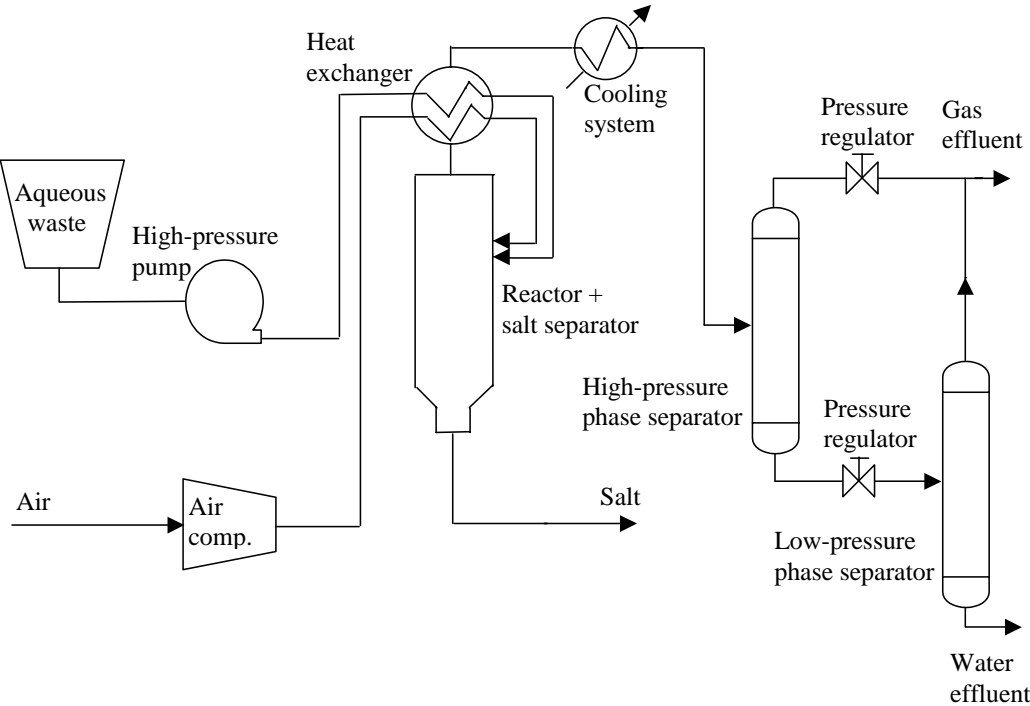


Fig. 6. Simplified diagram of a possible continuous flow SCWO system.

4.4. Requirements for large-scale operation

Proper design and development of the equipment are of major importance in scaling up the system for wastewater treatment [66, 127, 128]. In addition to reaction (residence) time, temperature and oxidant, various other parameters, such as reactor geometry, mixing of organic waste and oxidant, flow velocity and pattern, feed preheating, rate-controlling mechanism and scale-up in general, may affect the oxidation result. The nature of the wastewater, the process requirements and the local environmental conditions must be considered in choosing the reactor to be used. Furthermore, the process must be safe and environmentally acceptable. From the cost point of view, construction, operation and maintenance are of key importance. The biggest fixed cost is the plant itself. The major part of the operating costs is for the oxidant and energy. Operating costs are reduced with use of air, which is the cheapest oxidant. However, the compressor needed for the air adds to the capital costs.

Continuous flow systems are favoured in large-scale operation because no re-loading as in batch systems is required and both the waste treating capacity and efficiency are high. The larger the capacity of the equipment, and the higher the energy requirement, the more important is to save energy. Fortunately, the energy needed for heating can be reduced with use of heat exchangers. Also, a recycle stream of a portion of the effluent can be mixed with the feed streams to increase the temperature and ensure that the oxidation reaction is rapidly completed. It is also possible to expand the formed gas through a turbine to extract the available energy as power, which can be used for compressing the inlet air.

4.5. Problems related to SCWO and PHWO

SCWO and PHWO processes should be as simple as possible, reliable and economical. Because of the high temperature and pressure, the materials (reactor, tubes, joint parts) need to be durable – to avoid leaks, guarantee long lifetime and allow safe and efficient operation.

One of the greatest challenges is the corrosive nature of water at high pressure and temperature with some oxidant added. If the organics to be oxidized contain only C, H, O and N, no severe corrosion problems arise at longer service times [129]. Major problems arise, however, if acids are formed during the oxidation of organics containing hetero atoms. Corrosion is often greatest at temperatures slightly below the critical temperature of water because acids and bases are dissociated, leading to extreme values of pH [130-133]. Corrosion is usually lower under supercritical conditions because acids and bases

are less dissociated and the pH of the solution is closer to neutral. Oxides formed during reactions may improve the stability of the reactor materials by acting as protectants. Although some materials are more resistant to acid corrosion than others, one material alone will hardly withstand all acidic solutions [134, 135]. Nickel alloys (*e.g.* Hastelloy C-276, Inconel 600 and 625) are often used in SCWO, because they are considered relatively resistant to corrosion under supercritical conditions.

Control of precipitation of salts is of major importance because the precipitants may plug the reactor, even at high flow velocities. Various arrangements are available to overcome plugging problems. The solubility of most salts is increased with pressure and thus with density of the supercritical fluid [136, 137]. At the same time, however, the solubility of protecting oxides, and thus corrosion, is increased. Another approach is to cool the bottom zone of the reactor. Most of the precipitating salts will then be thrust into the cooled brine and can be collected from the outlet at the bottom of the reactor. The simplest and best way to overcome the plugging problem is to minimise the salt concentration of the influent.

4.6. Parameters affecting the oxidation

The PHWO/SCWO process is governed by numerous operational parameters, *e.g.* temperature, reaction (residence) time and oxidant concentration, which need to be optimized to obtain high destruction efficiencies for organics. The oxidation conditions are highly dependent on the type of organics in the waste. Stable aromatic compounds such as PCBs, dioxins and furans require more energy for complete destruction than do less stable aliphatic compounds. Choice of oxidant affects the oxidation result, and catalysts may decrease the amount of energy needed in the process. Under optimized conditions, almost 100% overall destruction of the organic compounds can be achieved.

4.6.1. Temperature, reaction time and pressure

Temperature and reaction (residence) time are strongly interrelated, and normally reaction times must be longer at lower temperatures. In most cases, temperature is chosen so that the rate of the oxidation reaction is high, and, with flow reactors, the volumetric flow can be kept high. Typical operating temperatures and reaction times in SCWO are 400-650°C and 10-30 s, respectively. In PHWO, temperatures are below the critical temperature of water and depend on the other parameters (*e.g.* use of a catalyst) affecting the oxidation efficiency. Organic concentration of the aqueous waste has a major effect on the heat production. Enough heat must be generated to maintain the reaction, but the wall temperature of the reactor must not exceed the limits of the material.

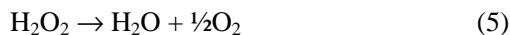
Preheating of the influents (oxidant and aqueous waste) can be applied to lower the energy needed in the reactor. However, total oxidation efficiency may be reduced, if the preheating time is too long or the temperature too high. This is, in the preheating tube, organics may be converted to stable organic products during thermal pyrolysis [138] or oxidant may be decomposed, lowering the amount of active radicals participating in the oxidation process [139] (see 4.6.2.).

Operating pressures should be high enough to prevent the water from vaporizing. In flow reactors, pressure has an effect on the residence times through the changes in volume and density of water. In practice, it has been observed that pressure has a slight effect on the conversion rates of organics in liquid or supercritical state, but this effect is considered to be smaller than that of temperature or reaction time [85, 140, 141]

4.6.2. Oxidant

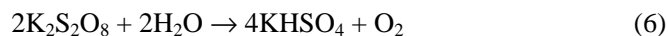
The oxidant for PHWO and SCWO, most commonly air or O₂, is normally used in stoichiometric excess to ensure effective and complete oxidation. As an operating cost, air is the most economical choice, but it must be compressed first. Oxygen is often fed to the reactor in liquid form, but there are also other possibilities for oxygen production. Misch *et al.* [126], for example, have produced oxygen for the treatment of contaminated soil by means of electrolysis. The oxidation reaction may start by activation of either the oxygen (electrophilic oxidation) or the hydrocarbon molecule (nucleophilic oxidation) [142]. Oxidation with oxygen generally follows the free-radical mechanism, but ionic mechanisms have also been proposed.

Hydrogen peroxide (H₂O₂) is another widely used oxidant. Hydrogen peroxide decomposes by the following reaction:



This reaction has been shown to proceed via free radicals OH and OH₂ [143-145]. The hydroxyl radical is one of the strongest inorganic oxidants. It has been suggested that hydrogen peroxide is important only at the onset of the reaction, where it reduces or even eliminates the induction step of the reaction.

Persulphate oxidations have been well studied [146, 147]. Potassium persulphate is an efficient inorganic oxidant at temperatures clearly below the critical temperature of water. It begins to react strongly at about 100°C forming sulphate radicals (rate determining step), which react with the organic compounds in a complex radical chain mechanism. In aqueous medium, potassium persulphate follows the decomposition reaction



Potassium persulphate has been used in the oxidation of various organics, including phenolic compounds, carboxylic acids and more complex organics, with and without a catalyst at temperatures below 100°C [148-150]. Propagation of the reaction is slow at room temperature, but with the help of a catalyst (*e.g.* silver) good results can be achieved under mild conditions. The oxidation efficiency of persulphate has also been exploited in the determination of organic carbon [151, 152]. Potassium persulphate has not been used as oxidant in continuous flow reactors under supercritical conditions. The sulphate released to water is a limiting factor when potassium persulphate is applied in wastewater treatment.

4.7. Other methods in comparison

Numerous physical, biological and chemical techniques are used in the treatment of wastewaters and sludges. Several review-type articles and books offer a good overview of the techniques [127, 153-155]. Some of the features of the alternative techniques, with a view to the features of SCWO and PHWO, are reported in the following.

High removal efficiencies for organic pollutants can be obtained by incineration. However, toxic organics such as PCDDs and PCDFs and some NO_x and SO_x compounds (not present in noticeable concentration in SCWO) may be released. Incineration thus requires an off-gas system to eliminate or reduce emissions. The temperatures used in the process are high (often 900 - 1300°C) and energy consumption, especially in large-scale operation, is higher than in SCWO.

Techniques such as soil vapour extraction, steam extraction and thermal desorption have been widely used in large-scale remediation of soil contaminated with organics. The gases formed must be eliminated; for example, they can be captured by active carbon or burned in an afterburner. Soil washing is a water-based process in which pollutants are removed from soils by mechanical scrubbing. The contaminated water used in the washing then requires further treatment, however. Stabilization and solidification have been used to minimise the risk of potential leaching of pollutants to the environment. Sedimentation (by gravitational settling) is one of the most widely used unit operations in wastewater treatment. Suspended particles that are heavier than water are separated from water by this technique. None of these techniques provides contaminant destruction and thus they cannot be described as a permanent solution.

Adsorption of organic pollutants onto active carbon is a widely used and effective technique, but expensive. To lower costs, the active carbon is often regenerated. Thermal regeneration requires very high temperatures, and other regeneration techniques, such as catalytic regeneration in PHW, have been tested. Membrane techniques (*e.g.* reverse osmosis, filtration techniques and sorptive/desorptive ion exchange membranes) are another alternative for improving the quality of water. Membrane techniques are used, for example, in desalting of brackish water and to remove dissolved solids from wastewater. In practice, membranes are seldom applied because replacement of the membrane tends to be expensive.

Biological methods take advantage of living organisms, typically bacteria and fungi. However, biological processes have the drawback that they are slow, do not allow high organic load and are not suitable for compounds that are toxic to the microorganisms. For example, aromatic compounds like phenols are considered to be toxic to microbial populations at high concentrations, and various halogenated organics are seldom removed efficiently. Furthermore, the sludge formed during biological treatment must be then disposed of either by landfilling or burning. The activated-sludge process is one of the most commonly applied biological techniques, taking advantage of aerobic bacterial culture.

Chemical treatment is often expensive, with generation of large volumes of organic waste, and it is frequently applied as a pretreatment step to reduce toxicity. Depending on the waste and the purpose of the detoxification, chemical treatment can be applied for pH adjustment, coagulation of colloidal impurities, precipitation of dissolved compounds, oxidation, reduction and sludge conditioning. Advanced oxidation processes (AOP) include, in addition to PHWO and SCWO, chemical oxidation and utilization of UV radiation together with hydrogen peroxide or ozone or some other oxidant.

5. PRESSURIZED HOT WATER EXTRACTION

Hot water ($T = 50\text{-}100^{\circ}\text{C}$) at atmospheric pressure has long been used in the extraction of organic, mainly relatively polar, compounds from solid matrices [156]. Hydrodistillation and steam extraction have been applied to volatile organic compounds [155]. Hawthorne *et al.* [157] were the first to fully exploit the altered physico-chemical properties of pressurized hot water in extraction processes. Other terms for pressurized hot water extraction (PHWE) are “subcritical water extraction”, “extraction with water at elevated temperatures and pressures”, “high temperature water extraction” and “extraction using hot compressed water”.

PHWE has been applied to the extraction of PAHs [158-161], PCBs [162, 163], phenols [157, 160], alkanes [160, 161] and PCDDs and PCDFs [164, 165] from solid matrices. Additionally, it has been used to extract pesticides [166, 167], essential oils [168, 169] and flavours [170, 171]. It has also been used in combination with other analytical techniques, such as solid phase microextraction (SPME) [172, 173] and LC-GC [174]. Some SFE applications have utilized SCW as extraction medium [157, 175, 176]. Because SCW provides a highly reactive environment, decomposition of compounds takes place more easily than in PHW, and thermostability of the compounds is important.

5.1. Pressurized hot water as extractant

The success of pressurized hot water extraction depends on the extraction conditions, the nature of the sample and the analytes to be extracted. Interactions between the analytes, the starting solid sample and water should be considered for optimal results. Fast diffusion, low viscosity and low surface tension are achieved in PHWE. The effects of increased solute vapour pressure and accelerated thermal desorption on recovery are significant owing to the high extraction temperature. PHWE, like many other extraction processes, comprises four steps: desorption, diffusion, dissolution and chromatographic elution out of the sample cell [34, 35, 59].

The initial desorption process is not well understood, but, for example, with real environmental samples it may control the overall extraction rate. Interactions between PHW and the sample matrix are important, though perhaps not so pronounced as in SFE with CO₂. PHW may alter the matrix by expanding or contracting it and thus affect the extraction speed and efficiency. Movement of the analyte from matrix to PHW is affected by diffusion and convection. In diffusion-limited extraction, decreasing the particle size (increasing the surface area) and/or increasing the temperature will improve the extraction rate. The solvent power of PHW is important in PHWE (Section 3.4.). The dielectric constant has often been considered a key parameter in interpreting solvent-solute interactions. Although solubility is rarely a limiting factor for extractions, problems may arise with highly contaminated samples and static mode extractions (solubility-limited extraction). In addition to solute-solvent interactions, physical sweeping and chemical reactions may occur.

5.2. Equipment used in PHWE

PHWE is often carried out in dynamic mode where water flows continuously through the extraction vessel. In static mode, the extraction vessel is pressurized, and the extraction is

carried out without letting the fluid flow out of the vessel. SFE and ASE instruments can both be used in PHWE, but their temperature maxima (in commercial instruments) are limited to 150 and 200°C, respectively. No dedicated instrument for PHWE is yet available commercially. The instrumentation (Fig. 7) resembles that of PHWO and SCWO systems. As there, the materials must withstand high temperatures and pressures. The main parts of continuous flow (dynamic mode) PHWE equipment are a high-pressure pump for water, a heating system, preheating tube, extraction vessel, cooling system, pressure or flow regulator and vessel or solid trap for sample collection.

High-pressure pumps should be capable of compressing the water to the required pressure. A heating oven, sand bath or resistive heating block can be used to heat the extraction vessel to the selected temperature. Stainless steel is the most common material for the extraction vessel, which is loaded with the sample and then closed. Vessels can be purchased or they can be made in the laboratory.

After exiting the heating system and before entering the pressure or flow regulator (*e.g.* a micro-metering valve), the hot water stream is cooled down, usually in cold water or an ice bath. Since analytes must be transferred out of the extraction vessel and collected quantitatively, after the PHWE experiment the tube leading from the vessel to the sample collection is flushed with an appropriate solvent. Analytes can be collected directly into the solvent and recovered by liquid-liquid extraction (LLE), or into a solid phase trap inserted between the cooling coil and the pressure regulator. Tenax, ODS and other SPE packings are common. After the trap has been dried, the analytes can be eluted with organic solvent. As discussed in Section 4.3., PHWE has also been connected on-line with oxidation in soil remediation; in that case, an oxidant inlet after the extraction step and a reactor are needed.

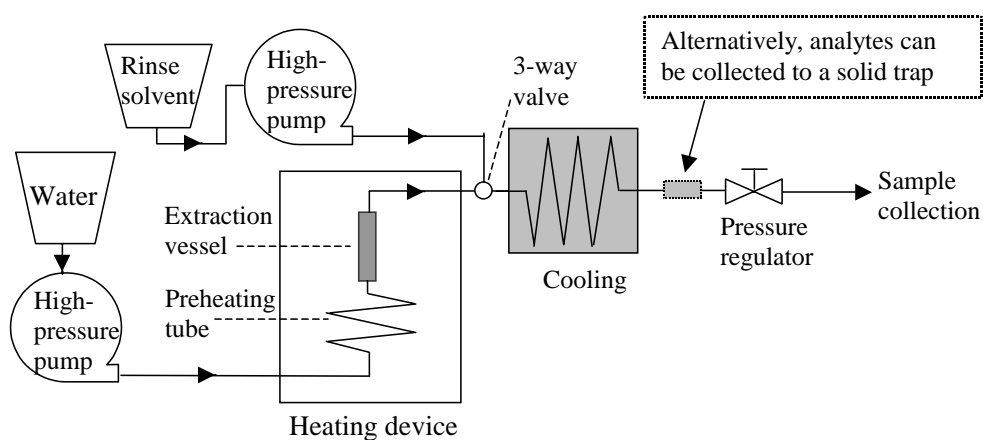


Figure 7. Typical PHWE equipment.

5.3. Problems related to PHWE

The relatively high temperatures may cause problems in PHWE. In some cases, analytes may react selectively with water during the extraction (*e.g.* hydrolysis). In addition, the organic compounds to be extracted may degrade more rapidly at elevated temperatures, substantially decreasing the recovery. Windal *et al.* [177], for example, found appreciable degradation of dioxins at 300°C. Sometimes degradation may affect the extraction process positively, for example, if the target analytes are thermally stable, while other, more labile compounds are degraded. High temperature may also cause structural changes in some matrices (*e.g.* synthetic polymers), which may affect the extraction process. At the high temperatures typical of PHW, special note must be taken of other compounds than analytes that may be extracted, leading to loss of selectivity. Finally, the higher the temperature and pressure, the more possible are leaks in the equipment reducing the reliability of the process.

5.4. Parameters affecting PHWE

The physico-chemical state of water, instrumental parameters and solute and solid (sample) characteristics all influence PHWE efficiency (Table 3). Sample pretreatment before extraction is essential especially with real soil samples.

5.4.1. Temperature and pressure

Temperature affects every step of the extraction (*i.e.* desorption, diffusion, dissolution and elution out of the sample cell). Extraction rate, efficiency and selectivity all are controlled by temperature. Increase in temperature enhances the vapour pressure and accelerates thermal desorption of the compounds, contributing to the extraction efficiency. The solubility of organic compounds may be strongly affected by temperature (Section 3.4.). Class-selective extractions can be performed in PHW because the solvent strength of water and the degree of the thermal effects can be adjusted with temperature. At higher temperature, the less the polar compounds are attracted by water and the efficiency of their extraction is increased. Yang *et al.* [160], for example, found that recoveries of non-polar PAHs and alkanes increased with a rise in temperature from 150 to 250°C.

In liquid phase, the effect of pressure on the dielectric constant and solvent strength is less than that of temperature, and thus exact pressure adjustment is not of first importance. In theory, nevertheless, both density and the dielectric constant of water are

increased with pressure and may affect the recovery. Non-polar organics are generally extracted more efficiently with steam than with liquid water because the dielectric constant of steam is close to unity. For example, Hartonen *et al.* [161] have found that better recoveries of PAHs are obtained with steam than with liquid water, and Yang *et al.* [160] have found the same for long-chain *n*-alkanes. Another reason for the better recoveries with steam may be that steam is diffused evenly through the sample, whereas liquid water flows along channels in the sample.

5.4.2. Extraction time, flow rate and extraction vessel

Maximum recovery of the organics is usually obtained in 10-20 min extraction time. After this, time has no essential effect on recoveries if temperature and pressure are optimized. However, in dynamic extraction mode, extraction efficiency of highly concentrated samples can be increased with flow rate. For example, Hawthorne *et al.* [157] have found that recoveries of PAHs and Yang *et al.* [160] that those of PAHs and alkanes increase with flow rate. Volume and geometry of the extraction cell may also affect the extraction process. Achievement of optimal recoveries depends upon the flow being in contact with the major area of the sample.

5.4.3. Sample and analyte to be extracted

Various sample properties (nature of matrix, porosity, surface to volume ratio, size) affect the extraction rate. Especially in diffusion-limited extractions, extraction rate increases with decreasing particle size and thus with increasing sample surface area. Accordingly, pretreatment of the sample (grinding, sieving, mixing with a solid, adjusting the pH) is important. Ease of separation will vary according to whether analytes are deposited in, adsorbed on or chemically bonded to the sample matrix. Also relevant are the location of the analytes and the porosity of the sample. Recoveries are usually better with porous samples and with analytes located at the surface. Recoveries are normally lower from real soil samples than from spiked samples because of the stronger matrix interactions. Polarity, volatility, molecular mass and the amount of analyte in the sample determine its solubility in PHW.

Table 3. Experimental variables affecting PHWE efficiency.

<i>Features of the solute</i> -analyte concentration, volatility, polarity and molecular mass	<i>Features of PHW</i> -temperature -pressure (density) and state of water (gas or liquid)
<i>Features of the solid sample</i> -sample and particle size -nature of the matrix -presence of other substances -pH of the sample	<i>Instrumental parameters</i> -extraction time -flow rate -overall volume of PHW -extraction vessel (size, geometry, void volume)

6. EXPERIMENTAL

6.1. Chemicals and solutions

Chemicals and materials used in the experiments (I-V) are listed in Table 4. The aqueous phenolic solutions (phenol, *m*-cresol, 2,3-dichlorophenol and 4-chloro-3-methylphenol as model pollutants, I-III) were prepared by weighing predetermined amounts of analytes into distilled deionized water and keeping the solution in an ultrasonic bath for 5-10 min. All the phenolics used in the experiments were soluble in water at working concentrations. Oxidant solution was prepared by weighing hydrogen peroxide (I, II, IV, V) or potassium persulphate (I, III) into distilled deionized water and shaking vigorously.

PAH stock solutions, prepared either in toluene and containing seven PAHs (IV) or in dichloromethane and containing six PAHs (V), were used in the PHWE-SCWO experiments with spiked sea sand (see Table 4 for details). The concentrations of PAHs were ca. 0.5 mg/ml (IV) or ca. 1.0 mg/ml (V). In addition, real soil from the site of a decommissioned coal gasification plant in Husarviken, Stockholm, was studied as solid sample (V) (see Table 4 for details). Quantitation was based on a PAH standard mixture. The extraction solvent in PHWE was distilled deionized water. The oxidant solution was prepared by weighing hydrogen peroxide into distilled deionized water.

Table 4. Chemicals and materials used in the experiments (I-V).

Compound	Manufacturer or supplier	Notes	Paper
Acetone	Lab-Scan, Analytical Sciences	For flushing the PHWE-SCWO equipment (99.8%)	IV, V
Barium chloride	E. Merck	For sulphate analysis (>99%)	III
Benzaldehyde	Local pharmacy	Reaction product (99%*)	IV
Benzoic acid	Local pharmacy	Reaction product (99%*)	IV
Benzyl alcohol	Merck	Reaction product (99%)	IV
1-Bromobenzene	Sigma Chemical CO	ISTD 2	III
2-Bromophenol	Fluka AG, Buchs SG	ISTD 2 (99%)	II
4-Bromophenol	Fluka AG, Buchs SG	ISTD 1 (99%)	II, III
4-Chloro-3-methylphenol	Fluka AG, Buchs SG	Model pollutant (99%)	II, III
<i>m</i> -Cresol	Fluka AG, Buchs SG	Model pollutant (>98%)	I
<i>p</i> -Cresol	Sigma Chemical Co.	Reaction product (99%)	IV
4,4'-Dibromooctafluorobiphenyl	Aldrich	ISTD (99%)	IV, V
Dichloromethane	Lab-Scan, Analytical Sciences	Solvent (HPLC grade)	I-V
2,3-Dichlorophenol	Fluka AG, Buchs SG	Model pollutant (\geq 97%)	I
Hexachlorobenzene	Sigma-Aldrich	ISTD 2 (99%)	I
Hydrogen peroxide	Riedel-de Haën	Oxidant (30% aq. sol.)	I, II, IV, V
Nickel(II) sulphate	E. Merck	For nickel analysis (>99%)	I-III
PAH standard mixture	AccuStandard, Inc.	17 PAHs (Z-014G-R), for identification and quantitation of PAHs	V
PAH stock solution	Self-made	Prepared in toluene or dichloromethane; PAHs: anthracene, chrysene, fluorene, naphthalene, perylene, phenanthrene and pyrene (not in Paper V)	IV, V
Pentachlorobenzene	Sigma-Aldrich	ISTD 1 (98%)	I
Phenol	Merck	Model pollutant and reaction product (>99.5%)	I, IV

Table 4, continued			
Potassium chloride	Riedel-de Haën	For sulphate analysis (>99.5%)	III
Potassium dichromate	E. Merck	For chromium analysis (analytical grade)	I-III
Potassium persulphate	E. Merck	Oxidant (99%)	I, III
Sea sand	Riedel-de Haën	Acid washed and calcined sea sand, grain size 0.1-0.3 mm	IV, V
Sodium sulphate	E. Merck	Calibration for sulphate analysis (>99%)	III
Soil	Supplied by Dr. Bert van Bavel (Umeå University, Sweden)	From decommissioned coal gasification plant in Husarviken, Stockholm; sifted through 4-mm sieve, homogenized and air-dried for three days; dry soil was ground to a fine powder in a ball mill; 79% dry subs. of which 29% org. carbon; contamination period 1893-1972	V
Toluene	Lab-Scan, Analytical Sciences	Solvent for PAHs in stock solution and for Soxhlet extraction	IV, V
Water	Distilled and deionized	PHWE solvent and solvent for model pollutants and for oxidants	I-V

*) Purity not indicated on label; determined by GC-MS in the laboratory

6.2. Equipment

The equipment used in PHWO and SCWO (I-III) is presented in Fig. 8 and that used in PHWE-SCWO (IV, V) in Fig. 9. Materials and devices are listed in Table 5.

6.2.1. Equipment for PHWO and SCWO

The high-pressure pumps were capable of pressurizing and transferring the aqueous solutions of oxidant and organics to the heated reaction zone for oxidation (Fig. 8). Studies were made with preheated (I, II) and non-preheated (I-III) tubes delivering the oxidant and organics. All tubes inside the heated oven were made of Inconel 600. Temperature was measured with two thermocouples installed on the reaction tube. Pressure (read on the pumps) was adjusted with a micro-metering high-pressure valve. Before collection of the sample, the effluent had to be cooled (cold water or ice bath) and depressurized. Possible insoluble particles were collected in a collector installed between the cooling bath and the pressure regulator to minimise the risk of blockage.

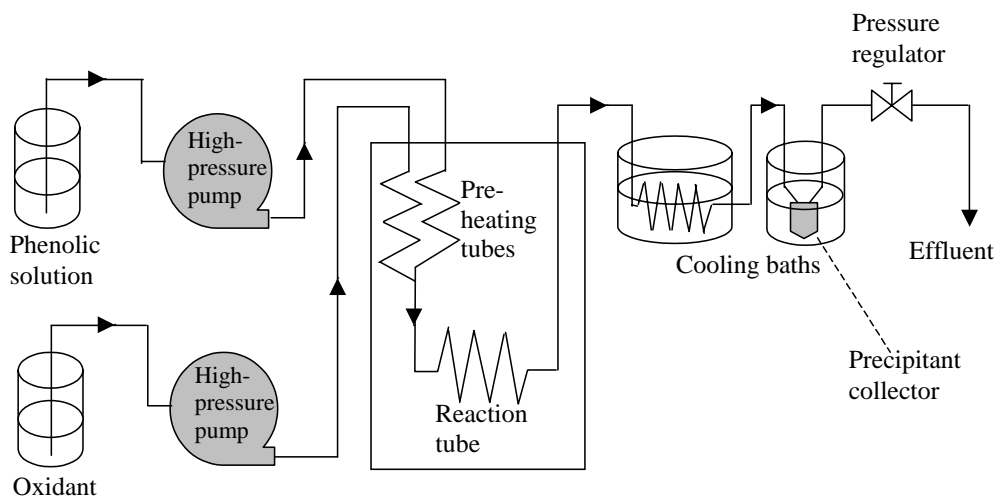


Figure 8. Equipment for PHWO and SCWO (I-III). Preheating tubes were used in some experiments (I, II).

6.2.2. Equipment for PHWE-SCWO

A high-pressure pump was used to pressurize and deliver water to the heated extraction vessel for extraction of organics from the solid sample (Fig. 9). The vessel was obtained from Keystone Scientific and made of stainless steel. Extraction temperature was measured by two thermocouples inserted near the extraction vessel. From the extraction vessel, the aqueous organic solution was delivered directly to the T-junction, where it was mixed with hydrogen peroxide, pumped by another high-pressure pump, ready for oxidation in the reaction tube. Oxidation temperature was read from a thermometer on the front panel of the heating oven and pressure from the digits on the pumps. All the tubes between the high-pressure pumps and pressure regulator were made of Inconel 600. The tube between the ovens was well insulated to prevent heat losses and guarantee quantitative transportation of the analytes in the aqueous solution to the reaction tube. Before sample collection, the effluent was cooled (cold water or ice bath) and depressurized (micro-metering high-pressure valve).

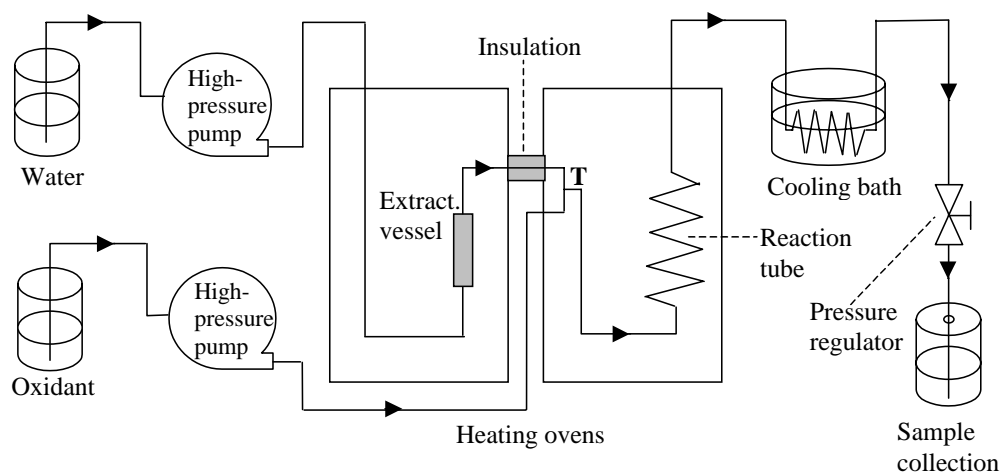


Fig. 9. PHWE-SCWO equipment (IV, V).

Table 5. Materials and devices used in the PHWO and SCWO (I-III) and PHWE-SCWO (IV, V) experiments. Instrumentation used in the sample analysis is included.

Material / equipment	Manufacturer and model / supplier	Notes	Paper
AAS	Perkin-Elmer 272	$\lambda(\text{Cr}) = 357.9 \text{ nm}$, $\lambda(\text{Ni}) = 232.0 \text{ nm}$	I-III
Autosampler	Hewlett-Packard 7636	Splitless injection (2.0 μl)	I-III
Autosampler	Hewlett-Packard 7636	On-column inj. (2.0 μl)	IV, V
Extraction vessel	Keystone Scientific Inc.	Stainless steel, V = 3.3 ml, 150 x 5.0 mm i.d.	IV
Extraction vessel	Keystone Scientific Inc.	Stainless steel, V = 2.2 ml, 100 x 5.0 mm i.d.	V
Gas chromatograph	Hewlett-Packard 5890		I-V
GC column	HNU-Nordion, NB-351	20 m x 0.2 mm i.d., phase nitroterephthalate modified polyethyleneglycol	I-III
GC column	BGB Analytik AG, BGB-5	20 m x 0.2 mm i.d., phase 5% diphenyl, 95% dimethylpolysiloxane	I
GC column	Hewlett-Packard, HP-5	25 m x 0.2 mm i.d., phase 5% diphenyl, 95% dimethylpolysiloxane	IV, V
Heating module	Pierce ReactiTherm	Sample concentration, N ₂ - evaporation + heating	I-V
Heating oven	Carlo Erba Fractovap model G1	Heating the reaction tube or the extraction vessel	I-V
Heating oven	Carlo Erba Series 2350	Heating the reaction tube in PHWE-SCWO	IV, V
High-pressure pump	Jasco PU-980	Delivering organics in PHWO/SCWO or water in PHWE-SCWO	I-V
High-pressure pump	LKB-2150	Delivering oxidant in PHWO/SCWO or PHWE- SCWO	I-V
Inconel 600	VICI AG Valco Int.	Reactor and pre-heating tube, 1.5 mm i.d	I-V
Mass spectrometer	Hewlett-Packard 5989A	EI ionization, 70 V, used in SCAN mode	I-V
pH meter	Jenway 3030		I-III

Table 5, continued			
Precipitant collector		Stainless steel	I-III
Pressure regulator	Jasco Inc.	Micro-metering high-pressure valve	I-V
Retention gap	BGB Analytik AG	2-3 m x 0.53 mm i.d., in GC DPTMDS–deactivated	I-V
Software for water properties	NIST/ASME, Standard Ref. Database 10, 2.01	Reaction time calculations	I-V
Software for GC-MS	Hewlett-Packard Chemstation	For GC-MS data analysis (incl. Wiley MS library)	I-V
Stainless steel capillary	Alltech Associates Inc.	Capillary after precipitant collector/pressure regulator, 0.5 mm i.d.	I-V
Thermometer	2 x Lutron TM-902C	Temperature control in PHWO/SCWO and PHWE	I-V
TOC analyser	Shimadzu TOC-5000	Method SFS-EN 1484	I, III, V

6.3. Procedures

6.3.1. Procedure for PHWO and SCWO

The following procedure was carried out to collect samples for GC-MS, corrosion and pH measurements:

- 1) Containers were filled with solutions of organics and oxidant.
- 2) High-pressure pumps delivering the solutions were launched at a selected flow rate.
- 3) Pressure was adjusted with a pressure regulator to the selected value.
- 4) Reference samples (3 x 10 ml for GC-MS analysis, and 1 x 10 ml for corrosion and pH measurements) were collected in 10 ml flasks at room temperature; no conversion for the phenolic compounds was assumed, which was also confirmed by tests.
- 5) The oven was heated to the selected temperature and allowed to stabilize for ~10 min.
- 6) 3 x 10 ml (I) or 4 x 10 ml (II, III) samples were collected in flasks for GC-MS analysis (RSDs were calculated to determine the repeatability); 1 x 10 ml sample was collected for corrosion and pH measurements.

7) The oven was heated to the next temperature needed for sample collection; samples were collected in the same way at each temperature.

8) The equipment was flushed with water at the highest sampling temperature, cooled down, and flushed with dichloromethane and/or acetone and water to avoid contamination in subsequent experiments.

The procedures for the collection of samples for TOC (I, III) and sulphate analysis (III) were similar to the procedures for GC-MS analysis and corrosion and pH measurements but were carried out separately. Three 10 ml aqueous samples were collected under each set of conditions.

6.3.2. Procedure for PHWE-SCWO

The following procedure was carried out to collect the samples for GC-MS:

1) Paper IV: about 4.5 g dry sea sand was weighed into the extraction vessel and 200 μ l of PAH stock solution (Table 4) was pipetted into the sand, which was allowed to stand for 1 or 20 h. Paper V: about 2.8 g sea sand was weighed into the extraction vessel, and 200 μ l of PAH stock solution (Table 4) was added to the sand, which was allowed to stand for 18 h; alternatively, 0.5 g contaminated soil and ca. 2.3 g sea sand (to fill the extraction vessel) were weighed into the vessel. In all cases, the organics were at the bottom of the extraction vessel.

2) Containers were filled with water (for extraction) and oxidant.

3) The oven for SCWO was heated to the selected temperature, oxidant flow was started and pressure was adjusted to the selected value.

4) The high-pressure pump delivering water to the extraction vessel and heating of the oven for PHWE were launched; effluent collection in dichloromethane ($V = 20$ ml) was started (the exit capillary was inserted in dichloromethane in the sampling bottle).

5) The oven for PHWE was heated to the selected temperature and the sample was collected for the selected extraction time; heating time to 200°C was ~8 min and to 300°C ~18 min, and these times were not included in the nominal extraction time (20 or 40 min, Paper IV, and 5 or 10 or 20 min, Paper V).

6) After the extraction, pumps were stopped and the ovens cooled down.

7) The tube from the T junction on was aerated and flushed with 40 ml of dichloromethane to sample collection.

8) The sample collection bottle was removed, the extraction vessel was replaced with a connection part and the tubes were flushed, through the pressure regulator, with acetone, dichloromethane and water.

Four experiments were carried out under each set of conditions (RSDs were calculated to determine the repeatability). PHWE experiments (without SCWO) were similar to the PHWE-SCWO experiments but water, instead of oxidant, was pumped at 385°C. TOC experiments (V) were carried out separately from the experiments for GC-MS. The procedure was similar to that described above except that dichloromethane was not used in the sampling bottle nor to flush the tube from the T junction to sample collection.

6.4. Experimental details

The experimental details of the PHWO and SCWO (I-III) and PHWE-SCWO (IV, V) experiments are given in Tables 6 and 7, respectively. Reaction time is often used with batch reactors, and residence time with tubular flow (plug flow) reactors, as a measure of the time that the solution spends inside the reactor [121, 178]. In Papers I and III-V, reaction time was the average time that the mixture of water, oxidant and organics spent in the reaction tube and was calculated by dividing the volume of the reaction tube by the average volumetric flow rate inside the reaction tube. The altered density and volume properties of the heated and pressurized water were taken into consideration in the calculations of flow rate. Note that the reaction temperature was measured on the surface of the reaction tube and the temperature of the aqueous solution inside the reaction tube may have been slightly different from this, with possible effect on the real reaction time (see 7.3.). In Paper III, contact time was used as a synonym of reaction time, describing the contact of the aqueous solution with the heated reaction tube. In place of reaction and contact times, space time was used in Paper II. Space velocity is defined as the ratio of the inlet volumetric flow rate at STP (0°C and 1 atm) to the volume of the reactor, and space time is the reciprocal of space velocity. Room temperature (ca. 25°C) was used instead of 0°C for reasons of convenience. Space time describes well the efficiency of the equipment in the treatment of wastewaters because it takes into account the inlet (pumping) flow rate at room temperature.

Table 6. Experimental details for PHWO and SCWO (I-III).

Parameter	Paper I	Paper II	Paper III
<i>Compounds to be oxidized and their concentrations</i>	Phenol, <i>m</i> -cresol and 2,3-dichlorophenol, <i>c</i> = 0.3 or 0.5 mM each	4-Chloro-3-methylphenol, <i>c</i> = 2.0 mM	4-Chloro-3-methylphenol, <i>c</i> = 2.0 mM
<i>Oxidants and their concentrations</i>	Hydrogen peroxide, <i>c</i> = 129 or 191 mM; potassium persulphate, <i>c</i> = 16.1 or 26.9 mM	Hydrogen peroxide, <i>c</i> = 320 mM	Potassium persulphate, <i>c</i> = 8.0 or 40.0 mM
<i>Temperature</i>	80-400°C	250-390°C	110-390°C
<i>Pressure and state of the reaction mixture</i>	220-310 bar Supercritical and liquid	4-311 bar Supercritical, liquid and vapour	235-310 bar Supercritical and liquid
<i>Reaction/space time</i>	Reaction time 4-57 s	Space time 10-60 s	Reaction time 3-59 s
<i>Volume of the reaction tube</i>	1.3 ml (no preheating), 2.0 ml (preheating)	1.3 ml	1.0 ml
<i>Volumes of the preheating tubes</i>	1.0 ml for the oxidant, 1.2 ml for the organics	0.65 ml for both H ₂ O ₂ and organics	No preheating

Table 7. Experimental details for PHWE-SCWO (IV, V).

Parameter	Paper IV	Paper V
Sample to be extracted	PAHs in toluene (<i>V</i> = 200 µl) spiked in sea sand	PAHs in dichloromethane (<i>V</i> = 200 µl) spiked in sea sand or soil sample
H ₂ O ₂ conc. in the pump and flow	5.6-112.6 g/l, 1.0 or 2.0 ml/min	2.7-26.6 g/l, 1.0 or 4.0 ml/min
Temperature in PHWE	T = 200 or 300°C	T = 150 or 300°C
Temperature in SCWO	T = 390 or 425°C	T = 385 or 425°C
Pressure	260 – 320 bar	265-320 bar
PHWE time	20 or 40 min	5, 10 or 20 min
Reaction time in SCWO	18-169 s	35-246 s
Volume of reaction tube in SCWO	1.8-11.3 ml	6.6-16.3 ml

During the experiments there was minor pressure fluctuation at some values (ca. ± 20 bar), especially in the vicinity of the critical point of water. This was considered unimportant since the state of the reaction mixture (supercritical, liquid or vapour) was not changed. Average pressure was calculated in each experiment, and this value was used in the calculations of water density and volume. Temperature was kept constant ($\pm 2^\circ\text{C}$) under each set of sampling conditions.

6.5. Pretreatment and analysis of the effluent

The instrumentation for the analysis of the effluent is described in Table 5. The basic tool for the analysis of the collected aqueous samples was GC-MS. This was used both in PHWO and SCWO (I-III) and in PHWE-SCWO (IV, V) experiments to determine the conversions and recoveries of the organics, and also those of other products formed in the oxidation. Identification of the compounds was based on the retention times and mass spectra (run in SCAN mode). The Wiley mass spectral library was used in the identification process. Total organic carbon analysis of the aqueous effluent was carried out with a TOC analyser (standard method SFS-EN 1484) (I, III, V).

6.5.1. Samples for PHWO and SCWO

Calibration for the organic model pollutants was generated from the GC-MS runs of dilution series of the compounds in dichloromethane. For the GC-MS experiments, dichloromethane was used in LLE of the collected PHWO/SCWO effluent. Two internal standards were applied in the sample analysis. After LLE, samples were concentrated by gentle nitrogen evaporation ($T=30^\circ\text{C}$) to the final volume of 1.5 ml, except (II, III) where a volume of 0.2 ml was applied as well. Splitless injection ($V = 2.0 \mu\text{l}$) and the following two columns were employed: semi-polar NB-351 (I-III) and non-polar BGB-5 (I). A DPTMDS-deactivated retention gap was used in front of the analytical column.

Corrosion (measured as nickel and chromium concentration of the effluent) was determined by AAS analysis of the aqueous effluent (I-III). The acidity of the effluent was measured with a pH meter. In sulphate analysis, potassium chloride was added to the effluent to prevent ionization interference. An accurately measured amount of barium chloride was added, distilled deionized water was added up to a constant volume and the samples were shaken vigorously. Sulphate was measured indirectly, as unreacted excess of barium by AAS.

6.5.2. Samples for PHWE-SCWO

Calibration for PAHs was generated from the GC-MS runs of a dilution series of the PAH stock solution (IV) or the PAH standard mixture (V). Calibration for quantitative analysis of other organics was similarly generated from a dilution series of the compounds.

Dichloromethane was used for LLE of the collected PHWE-SCWO effluent. The internal standard was used in sample analysis. After LLE, samples were concentrated by nitrogen evaporation ($T=30^{\circ}\text{C}$) to a final volume of 1.5 ml for GC-MS analysis. On-column injection ($V=2.0\ \mu\text{l}$) and a non-polar HP-5 column connected to a DPTMDS-deactivated retention gap were employed in GC-MS analysis. Soxhlet extraction was carried out with toluene as solvent (V). After extraction, ISTD was added, the sample was concentrated by rotavapor to ~ 10 ml and the final concentration to ~ 1.5 ml for GC-MS analysis was achieved by nitrogen evaporation. ASE analysis was carried out at Umeå University.

With spiked samples, recoveries of PAHs (and toluene in Paper IV) were obtained by comparing the amounts of PAHs (and toluene) determined in the PHWE-treated sample and the reference sample (200 μl of PAHs spiked in water, LLE-treated and analysed). In the experiments with the soil sample, recoveries of the PAHs obtained with PHWE were compared with those obtained with Soxhlet extraction (and ASE). Conversion of the PAHs in the PHWE-SCWO procedure was determined by comparing the amounts of PAHs found in the PHWE-SCWO-treated sample with those found in the PHWE-treated sample at 300°C and 20 min (V) or 40 min (IV) extraction time.

7. RESULTS AND DISCUSSION

Continuous flow PHWO and SCWO were applied to aqueous solutions containing phenolics as model pollutants (I-III). Effects of temperature, reaction time, oxidant concentration and preheating of the oxidant were investigated to determine the optimal oxidation conditions. Two oxidants, hydrogen peroxide and potassium persulphate, were compared. Study was also made of the corrosion, the pH and the reaction products formed during oxidation. PHWE-SCWO was used to extract organics, mainly PAHs, from spiked sea sand and real soil samples and to oxidize the compounds directly under supercritical conditions (IV, V). In PHWE, extraction time and temperature were investigated for their effect on extraction efficiency of PAHs. Recoveries obtained with PHWE were compared with those obtained with Soxhlet extraction and ASE. In PHWE-SCWO, the effects of temperature, reaction time and oxidant concentration on the removal of organics were studied. Also, reaction products formed in the oxidation were

analysed. Results obtained with PHWO/SCWO and PHWE-SCWO are described separately below.

7.1. PHWO and SCWO of aqueous phenolic solutions

7.1.1. Main parameters affecting the oxidation

PHWO and SCWO treatment of aqueous phenolic solutions is reported in Papers I-III. Under optimized conditions, excellent conversions were obtained for all compounds, with both hydrogen peroxide and potassium persulphate as oxidant. The main parameters affecting the oxidation efficiency, with both oxidants, were temperature and reaction time. Increasing these parameters enhanced conversions. Figure 10 presents the conversions of phenol, *m*-cresol and 2,3-dichlorophenol with potassium persulphate as oxidant at various reaction times as a function of temperature (I). Over 99% conversions were obtained in 55 s at 110°C, whereas only 9 s was needed for similar results at 178°C. Conversions of 2,3-dichlorophenol were slightly worse than those of the other compounds. The same results were obtained with hydrogen peroxide as oxidant (I).

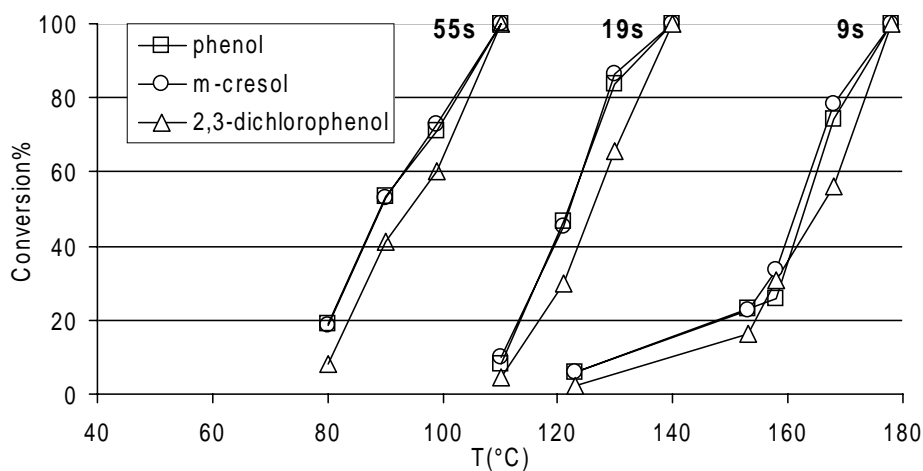
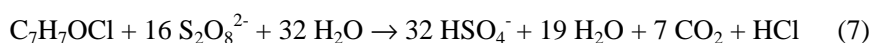


Figure 10. Conversions of phenol, *m*-cresol and 2,3-dichlorophenol ($c = 0.5$ mM each) in three reaction times as a function of temperature. Potassium persulphate was used as oxidant ($c = 26.9$ mM) (Paper I).

Oxidant concentration was also observed to affect the conversion. Better conversion of 4-chloro-3-methylphenol ($c = 2.0$ mM) was obtained at lower temperatures and shorter reaction times when potassium persulphate was used at a concentration of 40.0 mM rather than 8.0 mM (Fig. 11, Paper III). If we consider Eq. 7 as the reaction equation, we can see that the persulphate concentration of 40.0 mM was higher than the stoichiometric demand (32 mM). Persulphate concentration of 8.0 mM, on the other hand, was clearly lower than the stoichiometric demand, but nevertheless high enough to produce excellent conversions. 4-Chloro-3-methylphenol, for example, was destroyed with almost 100% efficiency in less than 40 s at 150°C. Goulden et al. [179] similarly report that the oxidation efficiency of nicotinic acid increased sharply with potassium persulphate concentration.



In experiments reported in Papers I and II, oxidant was used in amounts over the stoichiometric demand. Equations 8 and 9 describe the oxidation of phenol (I) and 4-chloro-3-methylphenol (II) with H_2O_2 .

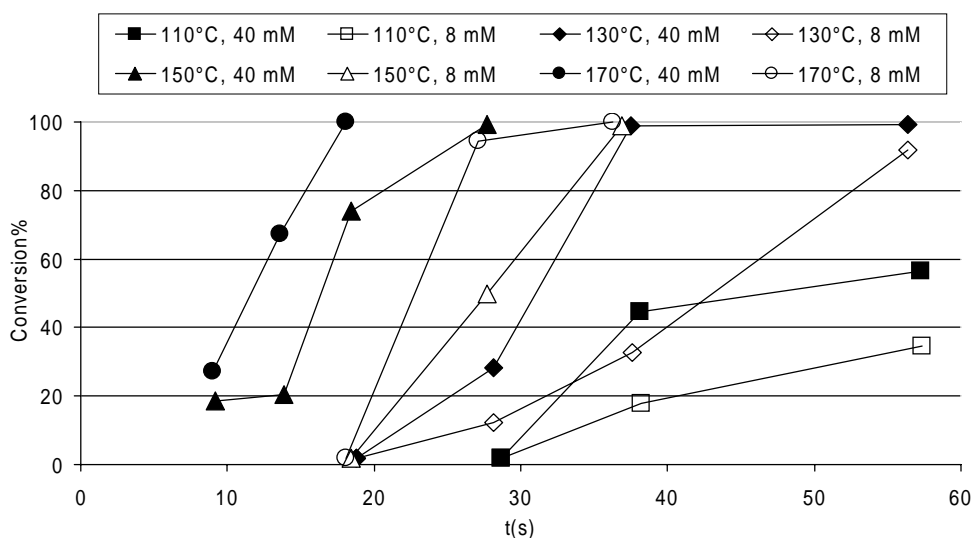
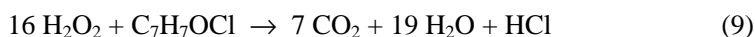
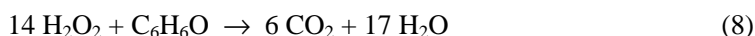


Figure 11. Conversion of 4-chloro-3-methylphenol ($c = 2.0$ mM) with potassium persulphate concentrations of 8.0 and 40.0 mM at various temperatures as a function of reaction time (Paper III).

It is better to describe the total oxidation efficiency as TOC removal rather than as conversion of a single compound, because all organic compounds (also possible reaction products and compounds that cannot be seen by GC-MS) are included in TOC. Clear reductions in TOC concentration were observed with both oxidants under various oxidation conditions (I, III). In oxidation of 4-chloro-3-methylphenol with potassium persulphate as oxidant, TOC concentration decreased sharply with increase in temperature from 120 to 200°C (Fig. 12, Paper III). After the temperature was further raised to 390°C, TOC removal was decreased somewhat, because reaction time was decreased with higher temperatures.

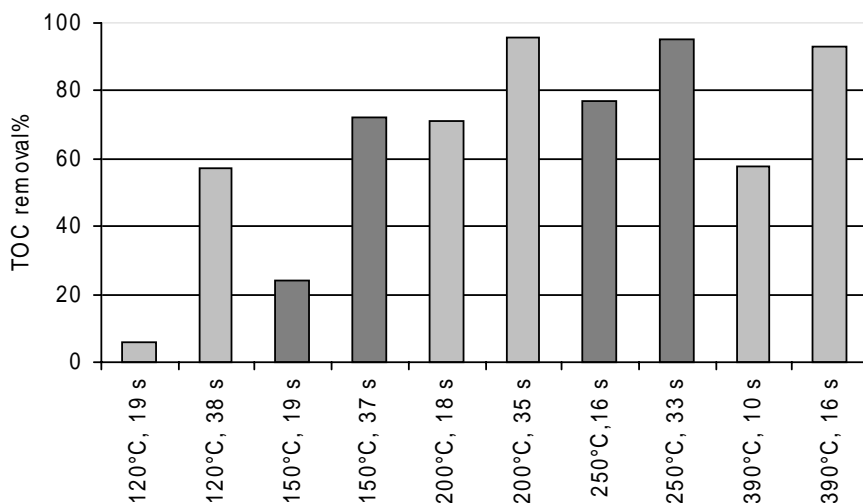


Figure 12. TOC removal, in oxidation of 4-chloro-3-methylphenol ($c = 2.0$ mM) with potassium persulphate concentration of 40.0 mM ($P = 251 - 310$ bar) (Paper III).

7.1.2. Comparison of oxidants

Good conversions of the phenolic compounds were obtained at lower temperatures with potassium persulphate than with hydrogen peroxide as oxidant. With hydrogen peroxide, temperatures as high as 320°C were required to achieve conversions of 4-chloro-3-methylphenol >98% (II), whereas with potassium persulphate temperatures below 150°C were sufficient for similar results (III). Figure 13 shows the conversions of phenol, *m*-cresol and 2,3-dichlorophenol at 248/249°C with hydrogen peroxide as oxidant relative to those obtained with potassium persulphate (I). At each reaction time, with potassium persulphate, the conversions of all phenolics were $\geq 99.8\%$. The high conversions obtained with potassium persulphate at moderate temperatures are due to the participation of reactive sulphate radicals in the complex radical chain mechanism.

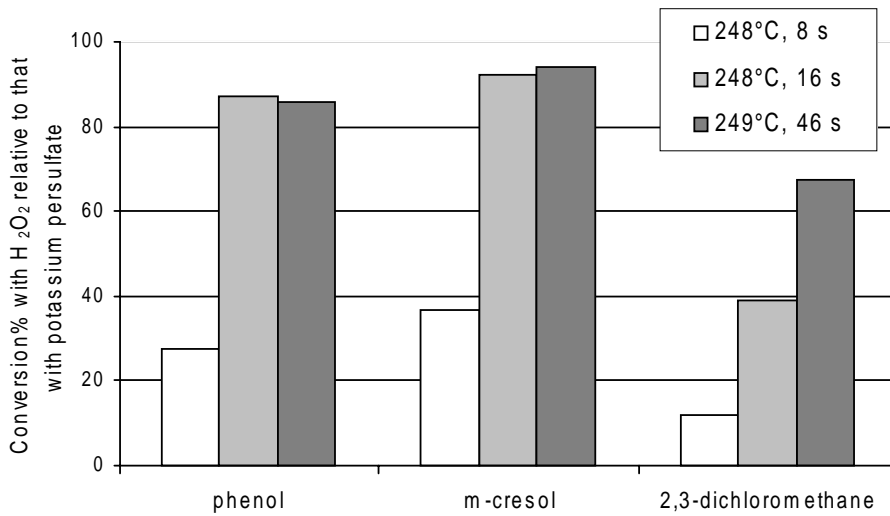


Figure 13. Conversions of phenol, *m*-cresol and 2,3-dichlorophenol ($c = 0.5$ mM each) at 248/249°C with hydrogen peroxide ($c = 191$ mM) as oxidant relative to conversions obtained with potassium persulphate ($c = 26.9$ mM). $P = 240$ - 260 bar (Paper I).

Figure 14 shows that, at lower temperatures, TOC was more efficiently removed with potassium persulphate than with hydrogen peroxide as oxidant (I). At 150°C, over 80% TOC removal was obtained with potassium persulphate but below 30% with hydrogen peroxide. The same maximum TOC removal (~94%) was obtained with both oxidants. However, with potassium persulphate this result was achieved at 250°C, whereas with hydrogen peroxide a temperature of 390°C was required. Under these conditions, with both oxidants, there was still some TOC left in the effluent. Probably, higher temperatures or catalysts would have provided maximum TOC removal.

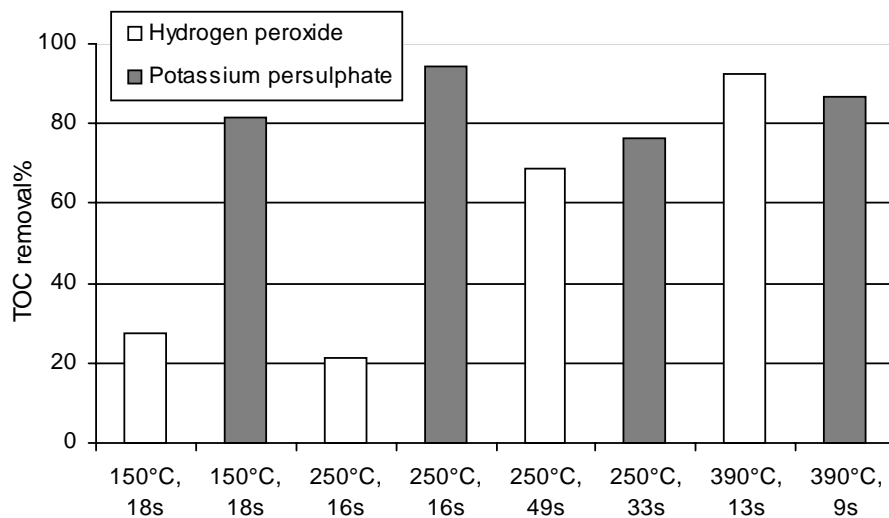


Fig. 14. TOC removal in oxidation of aqueous solution of phenol, *m*-cresol and 2,3-dichlorophenol ($c = 0.5$ mM each) with potassium persulphate ($c = 26.9$ mM) and hydrogen peroxide ($c = 191$ mM). $P = 220$ – 260 bar (Paper I).

A clear disadvantage of potassium persulphate is the released sulphate. The higher the temperature and the longer reaction time the greater was the amount of sulphate in the effluent (III). Almost stoichiometric amounts of released sulphate (~ 3500 mg/l) were observed in the effluent at 200 and 390°C. Thus, with potassium persulphate as oxidant, sulphate must be removed afterwards, for example, by precipitation, adsorption or ion exchange.

7.1.3. Preheating of the oxidant

With both oxidants, the conversions of the phenolics decreased overall when the tubes delivering organics and oxidant were preheated (I, II). Figure 15 shows the conversions of 4-chloro-3-methylphenol, with hydrogen peroxide as oxidant, with preheated and non-preheated tubes (II). Conversions were sharply decreased with the preheated tubes. Conversions of phenol, *m*-cresol and 2,3-dichlorophenol were likewise noticeably decreased with the same oxidant and preheating at 248/249°C (I). Evidently, with oxidant decomposed in the preheating tube, the contents of reactive hydroxyl radicals in the reaction mixture were lower, and so was the oxidation efficiency. It also can be concluded that the oxidation efficiency of oxygen (released when hydrogen peroxide is decomposed) is lower than that of hydrogen peroxide. Matsumura *et al.* [139] have found in SCWO of phenol that increasing the preheating time of hydrogen peroxide decreased

the destruction efficiency for phenol. In addition, Hatakeda et al. [180] have observed that hydrogen peroxide was significantly more effective than oxygen in SCWO of PCBs.

With potassium persulphate as oxidant and preheated tubes, the conversions of phenol, *m*-cresol and 2,3-dichlorophenol decreased significantly with increase in the oven temperature from $\sim 100^{\circ}\text{C}$ to 250°C [I]. This shows that potassium persulphate was increasingly decomposed at higher temperatures in the preheated tube, with negative effect on the conversions; that is, the amount of reactive sulphate radicals in the reaction mixture was lower with preheated oxidant. Preheating the oxidant at lower temperatures than that of the reaction temperature or using shorter preheating times would probably eliminate the decrease in conversion or even increase the conversion since the amount of energy required in the reaction tube is lower.

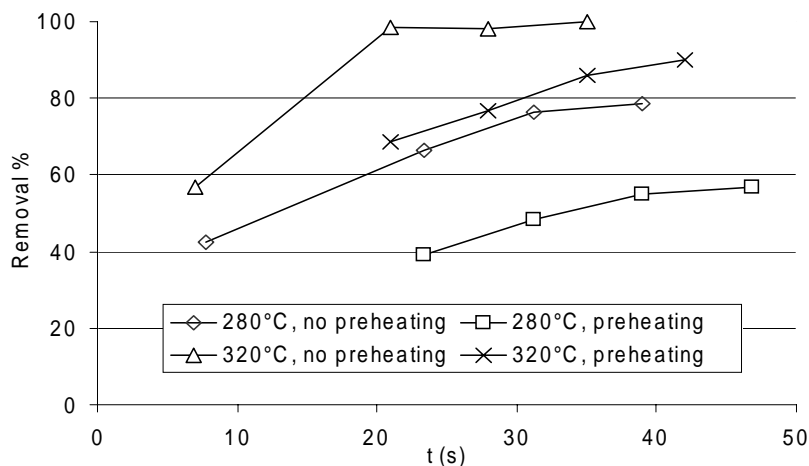


Fig. 15. Effect of preheating of hydrogen peroxide ($c = 320 \text{ mM}$) in the oxidation of 4-chloro-3-methylphenol ($c = 2.0 \text{ mM}$) at 280 and 320°C as a function of time. The preheating time was the as the reaction time (Paper II).

7.1.4. Oxidation in supercritical, liquid and gas state

No marked differences in the conversions of phenolics or TOC removals were observed when temperature was raised above the critical temperature of water (pressure higher than the critical pressure of water) (I-III). However, results were considerably different when 4-chloro-3-methylphenol was oxidized with hydrogen peroxide in gas phase rather than in supercritical or liquid state (II). Reaction times in steam ($<1 \text{ s}$) were only a fraction of those in liquid or supercritical state, and the conversions of 4-chloro-3-methylphenol were close to 100% at temperatures $>280^{\circ}\text{C}$. Obviously, the good results in steam are related to the high diffusivity and low dielectric constant. Furthermore, the

density of water and thus the concentration of organics are significantly decreased in steam and this may affect the oxidation process. In contrast to this, Thornton and Savage [85] have found that the time needed for 99.99% destruction of phenol at critical temperatures increases considerably when pressure is dropped so as to vaporize water. They concluded that the reaction rate constant is increased with temperature, but at the same time the density of the reaction medium and concentrations of the reactants are decreased. Near the critical point of water, the density decrease overwhelms the rate constant increase, and the time required to obtain 99.99% oxidation results increases. The authors note that the results are specific for the oxidation of relatively dilute phenolic streams and that results for other streams below the critical temperature of water may be different; for example, interphase transport limitations may occur. In our study in steam, conversion of 4-chloro-3-methylphenol dropped to below 20% when space time was decreased from 50 to 30 s. We would have expected a somewhat less dramatic drop in the oxidation efficiency.

7.1.5. Reaction products

The main reaction products (intermediates) in the oxidation of 4-chloro-3-methylphenol were studied with hydrogen peroxide and potassium persulphate as oxidant (II, III). With preheated hydrogen peroxide, the main reaction products reliably identified were 4-chlorophenol, 3-methylphenol and phenol (II). The amounts of the compounds, especially those of 4-chlorophenol, were clearly higher in steam than in liquid phase. When the oxidant was not preheated, only 4-chlorophenol was identified in the steam phase. Also some other reaction products were present in low abundance, especially in the steam phase, but they could not be reliably identified.

With potassium persulphate as oxidant, bis(2-ethylhexyl) ester of 1,2-benzenedicarboxylic acid was overall the most abundant reaction product in the oxidation of 4-chloro-3-methylphenol (III). At temperatures between 120 and 200°C it was present in relatively high concentrations at high TOC concentrations of the effluent, but at temperatures $\geq 250^\circ$ it was detected in only low concentration or not at all. Also 3-methylphenol and 2-methyl-1,4-benzenediol were identified as reaction products. However, they were present in only low concentration at the low temperatures and detected either in very small amount or not at all at $\geq 250^\circ\text{C}$. 4-Chlorophenol and phenol were not detected, in contrast to when hydrogen peroxide was used as oxidant. Surprisingly, intermediates like phenoxyphenols, biphenols, dibenzofurans, dibenzofuranols, dibenzodioxins and hydroquinones, which are common in the oxidation of phenols, were not found with either hydrogen peroxide or potassium persulphate as oxidant. Possibly higher initial concentrations of the organics would have resulted in positive detection.

7.1.6. Corrosion and pH

Some chromium and nickel were present in the effluent under all conditions (I-III). As shown in Fig. 16, nickel concentrations in the effluent were much higher with potassium persulphate than with hydrogen peroxide as oxidant. With potassium persulphate as oxidant, nickel concentration was maximum at 300°C (I), and nickel and chromium concentrations were relatively high at ~200-390°C (III). Surprisingly, with hydrogen peroxide as oxidant, nickel concentration of the effluent was maximum at 180°C in our first study (I, Fig. 16) but in other experiments both chromium and nickel concentrations generally increased with temperature, and values were maximum at 360 or 390°C (II). Several research groups have shown that corrosion tends to be greatest at temperatures somewhat below the critical temperature of water [130-133] (see also Section 4.5.). In our experiments, the highest temperatures ($T=390^{\circ}\text{C}$) were just a little above the critical temperature and it is possible that the metal concentrations would have decreased with further increase in temperature.

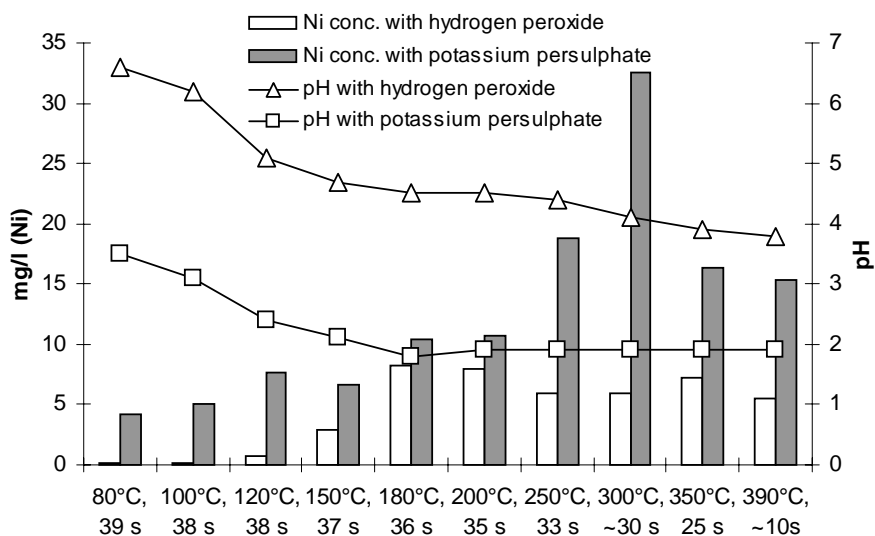


Fig. 16. Nickel concentrations and pH of the effluent in oxidation of a solution of phenol, *m*-cresol and 2,3-dichlorophenol ($c = 0.5 \text{ mM}$ each), with hydrogen peroxide ($c = 191 \text{ mM}$) and potassium persulphate ($c = 26.9 \text{ mM}$) as oxidant (Paper I).

With both oxidants, nickel concentrations of the effluent were higher in the oxidation of 4-chloro-3-methylphenol (II, III) than the oxidation of the mixture of phenol, *m*-cresol and 2,3-dichlorophenol (I). One reason for this may be that the concentration of 4-chloro-3-methylphenol ($c = 2.0 \text{ mM}$) was higher than that of 2,3-dichlorophenol ($c = 0.5 \text{ mM}$), *i.e.* the amount of chlorine and thus the concentration of hydrogen chloride in the effluent

were higher in the oxidation of 4-chloro-3-methylphenol. The corrosive effect of hydrogen chloride on nickel alloys (*e.g.* Inconel 600) at temperatures below the critical temperature of water has been shown by others [135, 136]. Thus, dissolution of the protective oxide layer may have contributed to the high concentrations of nickel in the effluent. In addition, the nickel concentration in the effluent is higher than that of chromium because the reaction tube material, Inconel 600, consists mostly of nickel (Ni > 72%, Cr ~ 15.5%). With hydrogen peroxide as oxidant, nickel and chromium concentrations of the effluent were significantly lower in steam phase than in liquid or supercritical state, and, in general, preheating of the oxidant decreased corrosion, probably because of the lower concentrations of reactive hydroxyl radicals in the reaction mixture (II).

In most cases, acidity of the effluent increased with temperature (I-III). Figure 16 shows this trend with both hydrogen peroxide and potassium persulphate as oxidant (I). In the oxidation of 4-chloro-3-methylphenol and 2,3-dichlorophenol the acidity can be explained by the formation of hydrogen chloride. In addition to this, acidic reaction products lower the pH. As can be seen in Fig. 16, corrosion was stronger at low pH values of the effluent. Moreover, pH values of the effluent were lower with potassium persulphate (lowest pH value 1.7, Paper III) than with hydrogen peroxide (lowest pH value 3.1, Paper II) and the corrosion was correspondingly greater. With potassium persulphate, hydrogen sulphate ($pK_a = 1.96$) was formed in the oxidation reaction (see Eq. 7) and it affected the pH of the effluent as well. Goulden and Anthony [179] also observed increased acidity with decomposition of persulphate.

Effect of pH on the efficiency of destruction of organics in PHWO and SCWO processes has rarely been studied. However, Kolaczkowski *et al.* [181] found that pH has a marked effect on the efficiency of destruction of phenol in WAO. Phenol was decomposed rapidly at pH ~4, but the destruction efficiency decreased noticeably when the pH was decreased to value of 2 or increased to value of 8-10. In our study and with hydrogen peroxide as oxidant, pH values of the effluent with high removal percentages of organics were about 4, which suggests that pH conditions were more or less optimal, at least for the oxidation of phenol. Nevertheless, it must be stressed that pH dependency is strongly case-sensitive and complex, and the nature of the organics and oxidant considerably affects the results.

7.2. PHWE-SCWO of solid samples

The success of the PHWE-SCWO process depends on the extraction efficiency in PHWE and the oxidation efficiency in SCWO. The compounds extracted from the vessel must be transferred quantitatively through the interface to the reaction tube.

7.2.1. Extraction with pressurized hot water

Figure 17 presents the effects of temperature and extraction time on the recoveries of PAHs. The RSDs of the results need to be taken into account in the evaluation. As can be seen, temperature had a marked effect on the recovery of PAHs. Recoveries, especially those of compounds of high molecular mass, increased when the temperature was raised from 150 to 300°C. This was mainly due to the higher solubility of the high molecular mass PAHs in PHW at 300°C. Hawthorne *et al.* [157] and Yang *et al.* [160] observed a similar temperature effect on recoveries. No marked differences in recoveries at 300°C were found between extraction times of 20 and 40 min (IV), but as can be seen in Fig. 17 the amounts of PAHs extracted were decreased somewhat when extraction time was reduced from 20 to 5 min (V). Increase in the extraction time from 20 to 40 min improved the recovery of toluene (from less than 70 to over 90%) probably because a large amount of toluene was present and the extraction was solubility limited (IV). Pressure was kept high enough to work in liquid state, and the effect was not studied in detail. Neither was the effect of flow rate studied.

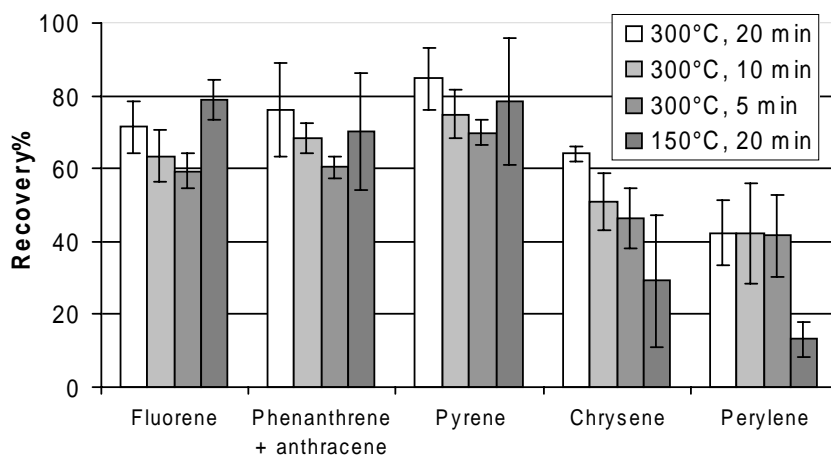


Fig. 17. Percentage recoveries of PAHs (RSDs marked as error bars), under various conditions, from spiked sea sand. Flow rate in PHWE was 1.0 ml/min. P = 260-320 bar (Paper V).

7.2.1.1. Spiked samples

The recoveries of PAHs from spiked samples at 300°C with 10-40 min extraction time were mostly in the range of ~60-80% (IV, V). Possibly some of the compounds were degraded during extraction because of the relatively high extraction temperature, and thus the amounts of organics remaining in the sand were smaller than the recoveries suggest.

As well, there may have been some losses of compounds during collection and sample treatment due to the high volatility of the PAHs. As an example of the effect of volatility, the recovery of naphthalene decreased from ca. 80% to 45% when the spiked sand was allowed to stand for 20 h instead of 1 h before the PHWE experiments (IV). In support of this, Hawthorne *et al.* [182] have recently reported that the high volatility of PAHs leads to significant losses during experiments. Clearly lowest recoveries were obtained for perylene, probably because of its high molecular mass and relatively low solubility in water. The recoveries of toluene (used as solvent for PAHs) were of similar magnitude to those of PAHs of low and medium molecular mass (IV).

7.2.1.2. Real soil samples

On average, PHWE (300°C, 20 min) gave better recoveries with soil samples than did 20 h Soxhlet extraction (Table 8, Paper V). In particular, the amounts of naphthalene and acenaphthylene extracted were considerably better, presumably because the low molecular PAHs are highly volatile and were lost during Soxhlet extraction or during rotavapor concentration of the sample. PHWE recoveries were also generally better than those of ASE (repeatability could not be estimated because only one experiment was carried out). Hawthorne *et al.* [158] found that the mean recoveries of PAHs of low and medium molecular mass were generally better with PHWE than with Soxhlet or ASE, but the recoveries of PAHs of high molecular mass were similar or even better with Soxhlet and ASE.

The colour of the Soxhlet extracts was dark brown, while that of the PHW extracts was orange/yellow, indicating that PHW worked more selectively (*i.e.*, not so much extracted from the sample matrix). This is in agreement with the observations of Hawthorne *et al.* [158]. Though PHWE is considered as a selective extraction technique, PAHs were not the only organics found after extraction of the soil sample (V). For example, 9H-fluoren-9-one, dibenzofuran, 9,10-anthracenedione and phenol were present in large amounts.

Though the recoveries of PAHs were high with PHWE, it can be assumed (on the basis of the results for the spiked samples) that the compounds were not totally extracted owing to matrix effects. In addition, some portion of the compounds may have been degraded, been lost during sample treatment or become stuck in the equipment. It should also be kept in mind that Soxhlet extraction and ASE do not give 100% recoveries (compared to the absolute true amounts of the compounds), even though these techniques are often used as reference methods for determining organics in soil samples. Analytes, sample matrix, temperatures and the solvents used in extraction all affect the results, and 100% recoveries may not be obtainable in practice.

Table 8. Extracted amounts of PAHs in $\mu\text{g/g}$ (%RSD) with ASE, Soxhlet extraction and PHWE under various conditions. Only one experiment was carried out with ASE. Nominal flow rate in PHWE was 1.0 ml/min (Paper V).

Compound	A	B	C	D	E
	ASE ¹ 150°C	Soxhlet 20 h toluene as solvent	PHWE 300°C 20 min $P = 290$ bar	PHWE 300°C 5 min $P = 295$ bar	PHWE 150°C 20 min $P = 300$ bar
Naphthalene	6.5	7.6 (22)	13.6 (22)	14.2 (9)	7.0 (22)
Acenaphthylene	23	15.2 (3)	58.6 (35)	53.4 (16)	10.2 (15)
Acenaphthene	1.6	4.4 (8)	4.6 (14)	3.2 (6)	3.2 (16)
Fluorene	23	31.8 (2)	35.0 (11)	32.0 (4)	29.8 (14)
Phenanthrene + anthracene ²	223	230.8 (5)	323.0 (4)	237.8 (12)	171.2 (17)
Fluoranthene	292	287.8 (4)	278.0 (2)	219.8 (6)	99.2 (27)
Pyrene	222	187.2 (1)	228.6 (2)	181.6(6)	76.2 (29)
Benzo(a)anthracene + chrysene ²	290	245.4 (6)	302.8 (0)	226.2 (12)	23.6 (42)
Benzo(b)fluoranthene + benzo(k)fluoranthene ²	208	195.6 (4)	255.0 (2)	187.8 (9)	12.0 (19)
Benzo(a)pyrene	178	159.8 (1)	175.6 (3)	94.8 (19)	3.2 (39)
Indeno(c,d)pyrene	88	76.8 (6)	89.4 (1)	73.6 (12)	2.0 (8)
Benzo(g,h,i)perylene	65	78.8 (4)	95.6 (3)	69.2 (12)	1.6 (15)

¹⁾ Quantitative analysis of PAHs in soil carried out at the University of Umeå (Sweden). ASE with hexane/acetone (1:1 v:v) at 150°C and 14 MPa. Evaporation, clean up through a silica column, elution with 25 ml hexane and 25 ml hexane/dichloromethane (3:2 v:v). Evaporation and change of the solvent to toluene. Analysis: HRGC/LRMS (Fisons GC 8000 / Fisons MD 800).

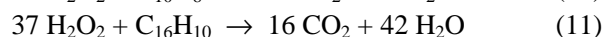
²⁾ Compounds were analysed as a single peak owing to poor chromatographic resolution

7.2.2. Conversions of PAHs in PHWE-SCWO

In all PHWE-SCWO experiments, pressure was high enough to keep the water in liquid (PHWE) or supercritical state (SCWO), and the effect of pressure on the results was not studied in detail (IV, V). In the experiments reported in Paper IV, only two temperatures of the reaction oven (390 and 425°C) were compared and temperature was found not to have a significant influence on the conversion of PAHs (Table 9). It is worth noting that reaction times decreased with increase in temperature and thus the conversions of PAHs were slightly decreased.

The conversions of PAHs with spiked sea sand sample and real contaminated soil are presented in Tables 9 and 10, respectively. The main parameters affecting the oxidation were reaction time and hydrogen peroxide concentration. Increasing the values of these parameters enhanced the conversions of PAHs (IV, V). Under the most drastic conditions, only small amounts of PAHs or no PAHs were found. With total flow of 5.0 ml/min, turbulence was created in the reaction tube (Reynolds number >2000), which enhanced mixing of the reaction mixture and also increased the conversion of the organics (Table 10). In the case of the spiked sample (IV), conversions of perylene (the PAH with the highest molecular mass) were the best, and in the case of the real soil sample (V), conversions of the PAHs with high molecular mass (*e.g.* benzo(a)pyrene, indeno(c,d)pyrene and benzo(g,h,i)perylene) were high as well. Bioremediation techniques were found to be more effective for PAHs with low molecular mass, and PAHs with more than four rings were even unaffected by these techniques [183, 184]. In this sense, SCWO is the more suitable technique for the destruction of PAHs as a whole.

It was assumed that the major part of the organics was extracted in the 10 ml (IV) or 20 ml (V) fraction during the PHWE process, and that the oxidant concentration was stoichiometrically sufficient (based on reaction equations) to oxidize all the organics. As an example, the oxidation reactions of naphthalene and pyrene are presented in Equations 10 and 11, respectively:



With the spiked sea sand, the equivalent oxidant concentration was calculated from the amounts of spiked PAHs (V) and toluene (IV). Toluene was much more abundant than PAHs and its concentration was used virtually alone in calculations of Paper IV. In studies with the real soil sample (V), the equivalent oxidant concentration was calculated from the amounts of PAHs found in ASE analysis. On the basis of these calculations, oxidant was used in stoichiometric excess to destroy organics effectively. With the real

soil, many other organics than PAHs were extracted as well, and from this it was assumed that the concentration of hydrogen peroxide was sufficient.

Even though hydrogen peroxide was used in high concentrations (Table 9, columns C-E) in studies with sea sand spiked with PAHs in toluene, there were still some PAHs and toluene left in the effluent (IV). Evidently, oxidant concentration was not at all times sufficient to oxidize all compounds. At 300°C, in general, the concentration of the organics was highest at the beginning of the nominal extraction time, and there may have been highly concentrated zones of organics in the extractant. In the case of the spiked sample, the amount of toluene was much greater than that of PAH, and the amount of hydrogen peroxide needed for the oxidation of PAHs was reduced. With the real soil sample, it is also possible that conversions of PAHs were lower due to the high concentrations of other organics (V). In addition, better conversions of PAHs probably would have been achieved at higher oxidation temperatures, but the technical limitations of the heating oven made further increase in temperature impossible.

Table 9. Percentage conversions of PAHs (%RSD) (PAHs in toluene spiked in sand) under various oxidation conditions. PHWE parameters: T = 300°C, t = 40 min, flow 1.0 ml/min and P = 265-320 bar. SCWO: total flow 2.0 (columns A-D) or 3.0 ml/min (column E), other parameters given in the table (Paper IV). ND = not detected.

Compound	A	B	C	D	E
	T = 390°C; c(H ₂ O ₂) = 5.6 g/l	T = 390°C; c(H ₂ O ₂) = 5.6 g/l	T = 390°C; c(H ₂ O ₂) = 56.3 g/l	T = 425°C; c(H ₂ O ₂) = 56.3 g/l	T = 425°C; c(H ₂ O ₂) = 112.6 g/l
Toluene	-	80.2 (28)	96.0 (1)	85.3 (2)	97.0 (2)
Naphthalene	11.3 (247)	65.7 (14)	98.8 (1)	94.8 (3)	98.4 (1)
Fluorene	46.2 (18)	81.7 (9)	98.8 (1)	95.7 (4)	98.3 (1)
Anthracene/ phenanthrene ^a	38.9 (17)	78.1 (7)	99.5 (0.4)	97.7 (2)	99.8 (0.2)
Pyrene	49.8 (16)	94.4 (2)	99.6 (1)	98.7 (2)	>99.9 (ND)
Chrysene	41.8 (19)	80.8 (10)	99.4 (1)	98.7 (2)	99.7 (0.3)
Perylene	81.0 (8)	99.5 (0.4)	99.5 (0.2)	99.3 (1)	>99.9 (ND)

^{a)} Compounds were analysed as one peak due to poor chromatographic resolution

Table 10. Percentage conversions of PAHs (%RSD) (real soil sample) under various oxidation conditions. PHWE conditions: T = 300°C, t = 20 min, flow 1.0 ml/min and P = 295–300 bar. SCWO conditions: total flow 2.0 (columns A-D) or 5.0 ml/min (column E), other parameters given in the table (Paper V).

	A	B	C	D	E
Compound	T = 425°C c(H ₂ O ₂) = 2.66 g/l t = 91 s	T = 425°C c(H ₂ O ₂) = 26.6 g/l t = 37s	T = 385°C c(H ₂ O ₂) = 26.6 g/l t = 246s	T = 425°C c(H ₂ O ₂) = 26.6 g/l t = 88 s	T = 425°C c(H ₂ O ₂) = 26.6 g/l t = 36 s
Naphthalene	75.6 (10)	80.0 (4)	80.2 (16)	90.0 (5)	91.9 (6)
Acenaphthylene	97.2 (0)	94.1 (3)	96.9 (1)	97.2 (0)	ND
Acenaphthene	63.6 (5)	ND ²	78.1 (2)	ND	ND
Fluorene	95.1 (1)	88.5 (2)	96.2 (3)	97.2 (1)	ND
Phenanthrene + anthracene ¹	91.3 (2)	93.2 (3)	96.9 (2)	99.1 (0)	ND
Fluoranthene	84.0 (5)	89.4 (6)	98.3 (1)	99.1 (1)	ND
Pyrene	94.1 (3)	94.1 (4)	99.3 (1)	99.7 (0)	ND
Benzo(a)anthracene + chrysene ¹	93.9 (2)	95.4 (3)	98.2 (1)	99.3 (0)	ND
Benzo(b)fluoranthene + benzo(k)-fluoranthene ¹	90.6 (2)	94.4 (4)	96.3 (1)	ND	ND
Benzo(a)pyrene	95.5 (0)	98.0 (2)	98.5 (1)	99.5 (0)	ND
Indeno(c,d)-pyrene	95.5 (1)	ND	ND	ND	ND
Benzo(g,h,i)-perylene	95.3 (1)	ND	ND	ND	ND

¹) Compounds were analysed as one peak due to poor chromatographic resolution
 ND (not detected) means that the compound was not found in the analysis

7.2.2.1. Additional organics

In PHWE-SCWO of spiked sea sand, conversions of toluene, which was used as solvent, were high and of the same magnitude as those of PAHs (Table 9, IV). With real soil samples the conversions of other compounds than PAHs present in the soil (*e.g.* 9H-fluorene-9-one, dibenzofuran, 9,10-anthracenedione and phenol) were high (V). With the highest oxidant concentration and total flow of 5.0 ml/min, only dibenzofuran was found in small amount.

In TOC experiments with the real soil sample, the TOC concentration of the effluent in PHWE-SCWO was decreased by as much as 91% relative to the concentration obtained in PHWE without the SCWO step (Fig. 18, Paper V). Under the same PHWE-SCWO conditions only naphthalene (Table 10, column E) and dibenzofuran were clearly detected, *i.e.* the chromatograms were almost clean. Because the amounts of naphthalene and dibenzofuran did not cover the remaining 9% of organics that, according to TOC analysis, were left in the effluent, there must have been some other organics left in the effluent. Probably not all the organics in the effluent (*e.g.* some high-molecular organics from the soil and reaction products formed during oxidation) could be seen by GC-MS.

Possibly, higher reductions in TOC concentration could be achieved at higher oxidant concentrations and temperatures. Problems in oxidation will arise if the organics enter the reaction tube in high concentration zones and the concentration of hydrogen peroxide is not then sufficient to oxidize all compounds. However, good oxidation efficiencies can be obtained without the oxidant concentration being as high as it was during the whole PHWE-SCWO procedure, because most of the organics are extracted at the beginning of PHWE. At the end of the extraction the concentration of the organics is lower, and so also the need for oxidant. No gradient in the oxidant concentration was developed because the extraction profile of the organics was not studied in detail.

In TOC experiments, the tube leading from the SCWO oven to sample collection was not flushed with dichloromethane to remove any remaining organics and this may have affected the TOC concentration of the effluent (V). The colour of the PHWE-SCWO effluent became lighter as the temperature and oxidant concentration were increased. At 425°C with hydrogen peroxide concentration of 26.6 g/l, there was no colour left in the effluent, indicating the destruction of colour-giving organics.

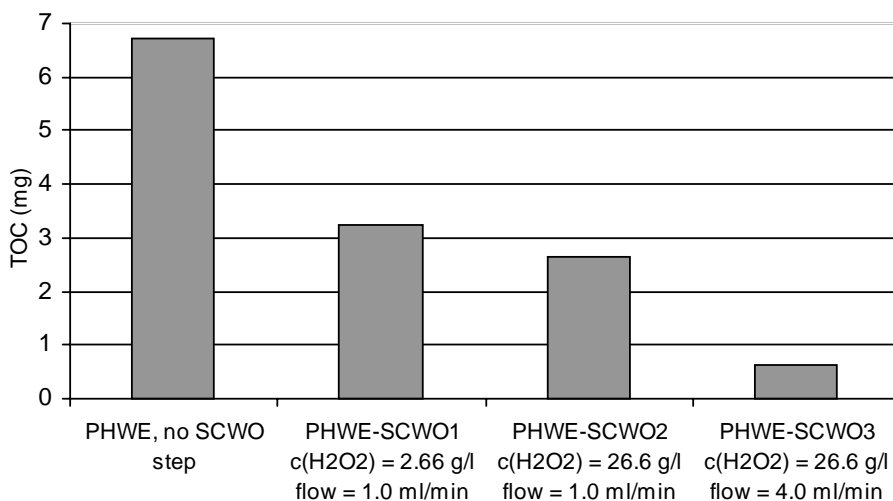


Fig. 18. TOC concentration of the effluent in PHWE-SCWO. P = 285-300 bar; PHWE: extraction time = 20 min, flow = 1.0 ml/min and temperature = 300°C; SCWO: T = 425°C, other parameters given in the figure (Paper V).

7.2.2.2. Reaction products

With both spiked samples (IV) and real soil (V), organics other than PAHs, formed as a result of oxidation, were found in GC-MS analysis. As can be seen in Fig. 19, with spiked samples, with toluene as solvent for PAHs, the most abundant reaction products overall were benzaldehyde and benzoic acid. All the compounds of Fig. 19 were also found in PHWE-SCWO of sand spiked solely with toluene (no PAHs). From this we can conclude that the main part of the reaction products was formed in the oxidation of toluene. The amount of benzoic acid was increased and that of benzaldehyde decreased with increased oxidant concentration and reaction time, probably because benzaldehyde was oxidized further to benzoic acid. Holliday *et al.* [185] also found benzaldehyde and benzoic acid as the reaction products in oxidation of toluene at temperatures below the critical temperature of water. In our experiments, in addition to the reaction products presented in Fig. 19, other compounds were found in low abundances, but they could not be reliably identified.

Benzoic acid and 9H-xanthen-9-one were not found in the analysis of the PHWE treated soil sample, but they were found in the PHWE-SCWO treated sample with oxidant concentrations of 2.66 and 26.6 g/l and oxidant flow of 1.0 ml/min indicating that they were formed during oxidation (V). They were not detected when the oxidant flow was increased to 4.0 ml/min, however, probably due to better mixing and higher concentration of the oxidant.

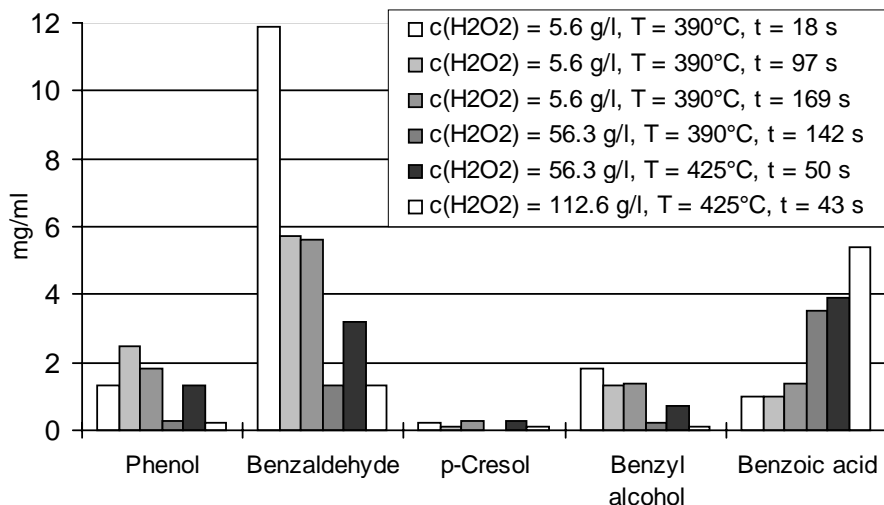


Fig. 19. Reaction products (mg/ml) formed under various oxidation conditions in PHWE-SCWO of spiked sea sand (PAHs in toluene). Nominal flow rate was 1.0 ml/min in extraction and 2.0 ml/min or 3.0 ml/min (with hydrogen peroxide concentration of 112.6 g/l) in oxidation. Extraction conditions: T = 300°C, t = 40 min, P = 265-320 bar (Paper IV).

7.3. Problems related to equipment and procedure

PHWO and SCWO and PHWE-SCWO equipment performed reliably most of the time. Malfunctions were similar in the two cases. Problems sometimes occurred with the pressure regulator, which became blocked. This was not more common with potassium persulphate than with hydrogen peroxide as oxidant, even though large amounts of sulphate were released in persulphate oxidation. Also, PHWE-SCWO experiments with real soil samples were carried out well, without major problems, despite the large amounts of organics extracted from the soil. Possibly some of the blockage was due to corrosion and release of metal particles from the walls of the reaction tube. Slight fluctuation in pressure (see Section 6.4.) may be related to partial blockage of the pressure regulator.

The reaction tubes broke a couple of times during the experiments. These situations were not dangerous despite the pressurized high temperature water. The vaporized water remained safely inside the reaction oven and there was no risk of personal injury.

To define the real volumetric flow velocity, and thus the reaction time inside the heated and pressurized reaction tube, was difficult. Even though the temperature of the outer wall of the reaction tube was known, the temperature profile of the aqueous solution inside the tube was not accurately registered. The greatest differences between the temperatures of the reaction tube wall and the aqueous solution inside the tube were probably at highest volumetric flow rates without preheated tubes. Consequently, the temperatures given must be taken as operational temperatures of the equipment and not as absolute temperatures of the reaction medium.

8. CONCLUSIONS

Laboratory-scale equipment for continuous flow PHWO and SCWO was constructed. Aqueous solutions of phenol, 2,3-dichlorophenol, *m*-cresol and 4-chloro-3-methylphenol were oxidized with potassium persulphate or hydrogen peroxide. The main parameters affecting the oxidation were temperature and reaction time.

Good oxidation results were obtained with both oxidants, but potassium persulphate was more effective at lower temperatures; for example, over 99% conversions of 4-chloro-3-methylphenol were obtained in less than 30 s at 150°C, but with hydrogen peroxide, similar results required temperatures well over 300°C. Over 90% removal of TOC was achieved with both oxidants, but again the required temperatures were again significantly lower with potassium persulphate. Applying higher temperatures than 200°C did not have a significant overall effect on the oxidation efficiency with potassium persulphate in the range of reaction times used, whereas the conversions of the organics and TOC removal were increased with temperature up to the supercritical region with hydrogen peroxide as oxidant. Corrosion (nickel and chromium concentrations of the effluent) was much greater with potassium persulphate than with hydrogen peroxide, being lowest in gas phase with hydrogen peroxide as oxidant. Technically, both oxidants were suitable for use in the continuous flow PHWO/SCWO equipment. Sometimes, the pressure regulator became blocked and it needed to be cleaned. Especially in large scale, a clear disadvantage of potassium persulphate is the sulphate released in the effluent. In wastewater treatment it would have to be removed by some method.

PHWO and SCWO studies in steam with hydrogen peroxide as oxidant showed that good conversions could be obtained for 4-chloro-3-methylphenol in very short reaction times. However, the reaction products (4-chlorophenol, 3-methylphenol and phenol) were clearly more abundant in steam than in liquid. Bis(2-ethylhexyl)ester of 1,2-benzenedicarboxylic acid, 3-methylphenol and 2-methyl-1,4-benzenediol were identified as reaction products in the oxidation of 4-chloro-3-methylphenol with potassium

persulphate. In most cases, preheating of the tube delivering potassium persulphate or hydrogen peroxide decreased the conversions of the organics probably due to the decomposition of the oxidant and partial loss of its activity in the oxidation tube. The amounts of reaction products of 4-chloro-3-methylphenol were also higher when the hydrogen peroxide was preheated.

On-line coupled PHWE-SCWO equipment was constructed. PAH-spiked sea sand and real contaminated soil were extracted with pressurized hot water and oxidized under supercritical conditions. In PHWE, the main parameter affecting the extraction efficiency was temperature. With spiked sea sand, ca. 70-80% recoveries were obtained for low and medium molecular mass PAHs at 300°C and 20 min extraction time. The recoveries were worst for the heaviest PAH, perylene. In PHWE of the real soil sample, the recoveries of the PAHs, especially those of naphthalene and acenaphthylene, were generally better than the recoveries obtained by ASE or Soxhlet extraction. Compared with ASE and Soxhlet extraction, a great advantage of PHWE is that no organic solvents are required during the extraction process.

In PHWE-SCWO, the hydrogen peroxide concentration and reaction time had a major effect on the oxidation efficiency. At 425°C with the highest oxidant concentrations, high conversions were obtained for PAHs with both spiked and real soil samples. Also the PAHs of highest molecular mass were effectively destroyed. Excellent conversions of other compounds than PAHs in the soil were obtained as well, and only small amounts of organics were found by GC-MS under optimized conditions. TOC concentration of the effluent (real soil sample) was decreased by ca. 91% relative to that obtained in PHWE without the SCWO step, indicating that some organics (not seen by GC-MS) were left in the effluent. Probably higher TOC removals would have been achieved at higher temperatures and/or oxidant concentrations. In practice, the PHWE-SCWO equipment performed reliably and safely despite temporary blockage of the pressure regulator.

9. REFERENCES

- [1] I. Asimov, *Asimov's Biographical Encyclopedia of Science and Technology*, Doubleday, Garden City, NJ, 1996
- [2] C. de LaTour, *Ann. Chim. Phys.* **21** (1822) 127
- [3] M. Faraday, *Phil. Trans. Roy. Soc.* **135** (1845) 155
- [4] T. Andrews, *Ann. Chim. Phys.* **21** (1870) 208
- [5] T. Andrews, *Proc. Roy. Soc. London* **24** (1876) 455
- [6] J. B. Hannay and J. Hogarth, *Proc. R. Soc. Sec. A* **29** (1879) 324
- [7] J. B. Hannay and J. Hogarth, *Chem. News* **41** (1880) 103
- [8] R. M. Smith, *Pure & Appl. Chem.* **65** (1993) 2397
- [9] P. W. Bridgeman, *Phys. Rev.* **3** (1914) 126, 153
- [10] O. Mishima and S. Endo, *J. Chem. Phys.* **68** (1978) 4417
- [11] J. D. van der Waals, *Die Kontinuität des flüssigen und gasförmigen Zustands*, Ph.D. Dissertation, University of Leiden, 1873; English translation: R. Threlfall, and J. Adair, in *Physical Memoirs*, Vol. 1, Part 3, London, 1890
- [12] Y. E. Gorbaty and G. V. Bondarenko, *J. Supercrit. Fluids* **14** (1998) 1
- [13] A. Kalaga and M. Trebble, *J. Chem. Eng. Data* **44** (1999) 1063
- [14] R. Biswas, J. E. Lewis and M. Maroncelli, *Chem. Phys. Lett.* **310** (1999) 485
- [15] E. U. Franck, *Endeavour* **27** (1968) 55
- [16] X. Lou, H. G. Janssen and C. A. Cramers, *J. Chromatogr. A* **785** (1997) 57
- [17] M. Ashraf-Khorassani and L. T. Taylor, *J. Chem. Eng. Data* **44** (1999) 1254
- [18] D. J. Miller and S. B. Hawthorne, *J. Chem. Eng. Data* **41** (1996) 779
- [19] Y. Yamini and N. Bahramifar, *J. Chem. Eng. Data* **45** (2000) 53
- [20] J. H. Hildebrand and R. L. Scott, *The Solubility of Nonelectrolytes*, Rheinhold Publishing Corporation, New York, 1950
- [21] R. C. Weast, M. J. Astle and W. H. Beyer (Eds.), *CRC Handbook of Chemistry and Physics*, 67th Edition, CRC Press Inc., Boca Raton, Florida, USA, 1987, p. C-732
- [22] J. C. Giddings, M. N. Myers, L. McLaren and R. A. Keller, *Science* **162** (1968) 67
- [23] M. Uematsu and E. U. Franck, *J. Phys. Chem. Ref. Data* **9** (1980) 1291
- [24] T. Kita, Y. Uosaki and T. Moriyoshi, in *High Pressure Liquids and Solutions*, Y. Taniguchi, M. Senoo and K. Hara (Eds.), Elsevier, Amsterdam, 1994
- [25] F. Stüber, A. M. Vázquez, M. A. Larrayoz and F. Recasens, *Ind. Eng. Chem. Res.* **35** (1996) 3618
- [26] J. T. Baker and M. A. Trebble, *Ind. Eng. Chem. Res.* **37** (1998) 1991
- [27] D. Q. Tuan, M. E. Yener, J. A. Zollweg, P. Harriott and S. S. H. Rizvi, *Ind. Eng. Chem. Res.* **38** (1999) 554
- [28] P. G. Debenedetti and R. C. Reid, *AIChE J.* **32** (1986) 2034
- [29] C. Kwag, C. W. Manke and E. Gulari, *J. Polym. Sci., Part B: Polym. Phys.* **37** (1999) 2771
- [30] K. H. Dudziak and E. U. Franck, *Ber. Bunsenges. Phys. Chem.* **70** (1966) 1120
- [31] R. A. Alberty, *Physical Chemistry*, 7th Edition, John Wiley & Sons, New York, 1987, p. 306
- [32] C. T. Lynch (Ed.), *Practical Handbook of Material Science*, CRC Press Inc., 1989

- [33] C. Wohlfarth and O. Madelung (Ed.), *Landolt-Börnstein Numerical Data and Functional Relationships in Science and Technology*, **Group IV, Vol. 6**, Springer-Verlag Berlin, Heidelberg, Germany, 1991
- [34] S. Bøwadt and S. B. Hawthorne, *J. Chromatogr. A* **703** (1995) 549
- [35] V. Janda, K. D. Bartle and A. A. Clifford, *J. Chromatogr.* **642** (1993) 283
- [36] M. Ashraf-Khorassani, M. T. Combs and L. T. Taylor, *J. Chromatogr. A* **74** (1997) 37
- [37] P. E. Savage, S. Gopalan, T. I. Mizan, C. J. Martino and E. E. Brock, *AIChE J.* **41** (1995) 1723
- [38] M. L. Lee and K. E. Markides, *Analytical Supercritical Fluid Chromatography and Extraction*, Chromatographic Conferences, Provo, Utah, 1990
- [39] J. R. Williams and A. A. Clifford, *Supercritical Fluid Methods and Protocols*, Humana Press, Totowa, New Jersey, 2000
- [40] P. G. Jessop and W. Leitner, (Eds.), *Chemical Synthesis Using Supercritical Fluids*, Wiley-VCH, Weinheim, Germany, 1999
- [41] R. E. Sievers and B. Hansen, *Chem. Eng. News* **69** (1991) 2
- [42] D. E. Raynie, *Anal. Chem.* **65** (1993) 3127
- [43] R. J. Chorley, in *Dictionary of Scientific Biography*, **Vol. III**, C. C. Gillispie (Ed.), Charles Scribner's Sons, NY, 1971, p. 586
- [44] C. Friedel and E. Sarasin, *Bull. Soc. Min.* **2** (1879) 113
- [45] C. Friedel and E. Sarasin, *Compt. Rend.* **97** (1883) 290
- [46] D. Stoye, in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th Ed., **Vol. A24**, Solvents, B. Elvers, S. Hawkins, W. Russey, and G. Schulz (Eds.), VCH Publishers, Inc., Weinheim, Germany, 1993, p. 437
- [47] K. Heger, M. Uematsu and E. U. Franck, *Ber. Bunsenges. Phys. Chem.* **84** (1980) 758
- [48] N. Yoshii, S. Miura and S. Okazaki, *Chem. Phys. Lett.* **345** (2001) 195
- [49] A. S. Quist and W. L. Marshall, *J. Phys. Chem.* **69** (1965) 3165
- [50] E. U. Franck, S. Rosenzweig and M. Christoforakos, *Ber. Bunsenges. Phys. Chem.* **94** (1990) 199
- [51] E. Wasserman, B. Wood and J. Brodholt, *Ber. Bunsenges. Phys. Chem.* **98** (1994) 906
- [52] M. M. Hoffmann and M. S. Conradi, *J. Am. Chem. Soc.* **119** (1997) 3811
- [53] Y. E. Gorbaty and A. G. Kalinichev, *J. Phys. Chem.* **99** (1995) 5336
- [54] A. G. Kalinichev and J. D. Bass, *J. Phys. Chem. A* **101** (1997) 9720
- [55] M. Nakahara, N. Matubayasi, C. Wakai and Y. Tsujino, *J. Molecul. Liq.* **90** (2001) 75
- [56] T. I. Mizan, P. E. Savage and R. M. Ziff, *J. Phys. Chem.* **100** (1996) 403
- [57] C. C. Liew, H. Inomata, K. Arai and S. Saito, *J. Supercrit. Fluids* **13** (1998) 83
- [58] M.-C. Bellissent-Funel, *J. Molecul. Liq.* **90** (2001) 313
- [59] M. D. Luque de Castro, M. Valcárcel and M. T. Tena, *Analytical Supercritical Fluid Extraction*, Springer-Verlag, Berlin Heidelberg, 1994, p. 101
- [60] S. Kim and K. P. Johnston, *Ind. Eng. Chem. Res.* **26** (1987) 1206
- [61] S. Kim and K. P. Johnston, *AIChE J.* **33** (1987) 1603
- [62] H. D. Cochran, P. T. Cummings and S. Karaborni, *Fluid Phase Equilibria* **71** (1992) 1

- [63] P. E. Savage, *Chem. Rev.* **99** (1999) 603
- [64] M. Modell, in *Standard Handbook of Hazardous Waste Treatment and Disposal*, H. M. Freeman (Ed.), McGraw-Hill, New York, USA, 1989, Section 8.11, p. 153
- [65] E. F. Gloyna and L. Li, *Waste Manage.* **13** (1993) 379
- [66] H. E. Barner, C. Y. Huang, T. Johnson, G. Jacobs, M. A. Martch and W. R. Killilea, *J. Hazard. Mat.* **31** (1992) 1
- [67] L. T. Boock, C. LaMarca and M. T. Klein, *Endeavour, New Ser.*, **17** (1993) 180
- [68] E. F. Gloyna and L. Li, *Environ. Prog.* **14** (1995) 182
- [69] J. W. Tester, H. R. Holgate, F. J. Armellini, P. A. Webley, W. R. Killilea, G. T. Hong and H. E. Barner, *Emerging Technologies in Hazardous Waste Management III*, ACS Symp. Ser. 514, American Chemical Society, Washington DC, USA, 1993, p. 35
- [70] N. L. Dickinson, U.S. Pat. 4,292,953 (1981)
- [71] T. B. Thomason and M. Modell, *Hazard. Waste* **1** (1984) 453
- [72] Z. Y. Ding, M. A. Frisch, L. Li and E. F. Gloyna, *Ind Eng. Chem. Res.* **35** (1996) 3257
- [73] Y. I. Matatov-Meytal and M. Sheintuch, *Ind Eng. Chem. Res.* **37** (1998) 309
- [74] P. E. Savage and M. A. Smith, *Environ. Sci. Technol.* **29** (1995) 216
- [75] J. C. Meyer, P. A. Marrone and J. W. Tester, *AIChE J.* **41** (1995) 2108
- [76] Z. Y. Ding, L. Li, D. Wade and E. F. Gloyna, *Ind. Eng. Chem. Res.* **37** (1998) 1707
- [77] P. A. Webley, J. W. Tester and H. R. Holgate, *Ind. Eng. Chem. Res.* **30** (1991) 1745
- [78] E. E. Brock, Y. Oshima, P. E. Savage and J. R. Barker, *J. Phys. Chem.* **100** (1996) 15834
- [79] P. Dagaut, M. Cathonnet and J.-C. Boettner, *J. Supercrit. Fluids* **98** (1996) 33
- [80] H.-J. Bleyl, J. Abeln, N. Boukis, H. Goldacker, M. Kluth, A. Kruse, G. Petrich, H. Schmieder and G. Weigand, *Sep. Sci. Technol.* **32** (1997) 459
- [81] S. Gopalan and P. E. Savage, *AIChE J.* **41** (1995) 1864
- [82] M. Krajnc and J. Levec, *AIChE J.* **42** (1996) 1977
- [83] C. J. Martino and P. E. Savage, *Ind. Eng. Chem. Res.* **36** (1997) 1391
- [84] J. R. Portela, E. Nebot, E. Martínez de la Ossa, *Chem. Eng. J.* **81** (2001) 287
- [85] T. D. Thornton and P.E. Savage, *AIChE J.* **38** (1992) 321
- [86] Y. Oshima, K. Hori, M. Toda, T. Chommanad and S. Koda, *J. Supercrit. Fluids* **13** (1998) 241
- [87] K. Hatakeda, Y. Ikushima, S. Ito, N. Saito and O. Sato, *Chem. Lett.* **3** (1997) 245
- [88] B. R. Foy, K. Waldthausen, M. A. Sedillo and S. J. Buelow, *Environ. Sci. Technol.* **30** (1996) 2790
- [89] S. F. Rice and R. R. Steeper, *J. Hazard. Mater.* **59** (1998) 261
- [90] G. Anitescu and L. L. Tavlarides. *Ind. Eng. Chem. Res.* **39** (2000) 583
- [91] P. C. Dell'Orco, E. F. Gloyna and S. J. Buelow, *Ind. Eng. Chem. Res.* **36** (1997) 2547
- [92] P. I. Proesmans, L. Luan and S. J. Buelow, *Ind. Eng. Chem. Res.* **36** (1997) 1559
- [93] D. S. Lee, K. S. Park, Y. W. Nam, Y.-C. Kim and C. H. Lee, *J. Hazard. Mater.* **56** (1997) 247
- [94] L. Li, E. F. Gloyna and J. E. Sawicki, *Water Environ. Res.* **65** (1993) 250

- [95] M. Goto, T. Nada, A. Ogata, A. Kodama and T. Hirose, *J. Supercrit. Fluids* **13** (1998) 277
- [96] T. Mizuno, M. Goto, A. Kodama and T. Hirose, *Ind. Eng. Chem. Res.* **39** (2000) 2807
- [97] M. Modell, J. Larson and S. F. Sobczynski, *Tappi J.* June (1992) 195
- [98] C. A. Blaney, L. Li, E. F. Gloyna and S. U. Hossain, *Innovations in Supercritical Fluids: Science and Technology*, ACS Symp. Ser. 608, American Chemical Society, Washington DC, USA, 1995, p. 444
- [99] J. B. Johnston, R. E. Hannah, V. L. Cunningham, B. P. Daggy, F. J. Sturm and R. M. Kelly, *Bio/Technology* **6** (1988) 1423
- [100] A. Shanableh and E. F. Gloyna, *Water Sci. Technol.* **23** (1991) 389
- [101] R. Li, P. E. Savage and D. Szmukler, *AIChE J.* **39** (1993) 178
- [102] T. D. Thornton, D. E. LaDue III and P. E. Savage, *Environ. Sci. Technol.* **25** (1991) 1507
- [103] M. Krajnc and J. Levec, *Ind. Eng. Chem. Res.* **36** (1997) 2451
- [104] E. E. Brock and P.E. Savage, *AIChE J.* **41** (1995) 1874
- [105] N. Crain, S. Tebbal, L. Li and E. F. Gloyna, *Ind. Eng. Chem. Res.* **32** (1993) 2259
- [106] V. S. Mishra, V. V. Mahajani and J. B. Joshi, *Ind. Eng. Chem. Res.* **34** (1995) 2
- [107] W. M. Copa and W. B. GitcheI, in *Standard Handbook of Hazardous Waste Treatment and Disposal*, H. M. Freeman (Ed.), McGraw-Hill, New York, USA, 1989, Section 8.6, p. 77
- [108] L. A. Pradt, *Chem. Eng. Prog.* **68** (1972) 72
- [109] F. Luck, *Cat. Today* **27** (1996) 195
- [110] G. H. Teletzke, *Chem. Eng. Prog.* **60** (1964) 33
- [111] F. J. Zimmermann, U.S. Pat. 2,824,058 (1958)
- [112] F. J. Zimmermann and D. G. Diddams, *Tappi* **43** (1960) 710
- [113] R. W. Strehlenert, Swed. Pat. 34 941, Sept. 1911
- [114] M. Chakchouk, M. Hamdi, J. N. Foussard and H. Debellefontaine, *Environ. Technol.* **15** (1994) 323
- [115] S. H. Lin and T. S. Chuang, *Toxicol. Environ. Chem.* **44** (1994) 243
- [116] J. N. Foussard, H. Debellefontaine and J. Besombes-Vailhe, *J. Environ. Eng.* **115** (1989) 367
- [117] S. H. Lin and Y. F. Wu, *Environ. Technol.* **17** (1996) 175
- [118] S. H. Lin and S. J. Ho, *Appl. Catal. B* **9** (1996) 133
- [119] J. B. Joshi, Y. T. Shah and S. J. Parulekar, *Indian Chem. Eng.* **27** (1985) 3
- [120] H. Ohta, S. Goto and H. Teshima, *Ind. Eng. Chem. Fundam.* **19** (1980) 180
- [121] Coulson & Richardson's Chemical Engineering, J. F. Richardson, and D. G. Peacock (Eds.), Vol. 3., 3rd Ed., Pergamon Press, 1994, New York, USA, p. 3
- [122] O. Levenspiel, *Chemical Reaction Engineering*, 2nd ed., John Wiley & Sons, 1972, NY, USA, p. 39
- [123] S. Goto, J. Levec and J. M. Smith, *Catal. Rev.-Sci. Eng.* **15** (1977) 187
- [124] C. N. Staszak and K. C. Malinowski, *Environ. Prog.* **6** (1987)39
- [125] A. Kruse and H. Schmieder, *Environ. Prog.* **14** (1998) 234
- [126] B. Misch, A. Firus and G. Brunner, *J. Supercrit. Fluids* **17** (2000) 227
- [127] Wastewater Engineering, Treatment, Disposal and Reuse, Metcalf & Eddy, Inc., Int. ed., 1991, p. 765

- [128] P. Kritzer and E. Dinjus, *Chem. Eng. J.* **83** (2001) 207
- [129] P. Kritzer, N. Boukis and E. Dinjus, *J. Mater. Sci. Lett.* **18** (1999) 1845
- [130] L. B. Kriksunov and D. D. MacDonald, *J. Electrochem. Soc.* **142** (1995) 4069
- [131] R. M. Latanasion, *Corrosion* **51** (1995) 270
- [132] D. B. Mitton, J.-H. Yoon, J. A. Cline, H.-S. Kim, N. Eliaz and R. M. Latanasion, *Ind. Eng. Chem. Res.* **39** (2000) 4689-4696
- [133] P. Kritzer, N. Boukis and E. Dinjus *Corrosion* **54** (1998) 824
- [134] P. Kritzer and N. Boukis, *J. Supercrit. Fluids* **15** (1999) 205
- [135] P. Kritzer, N. Boukis and E. Dinjus, *Corrosion* **56** (2000) 1093
- [136] S. T. Cui and J. G. Harris, *J. Phys. Chem.* **99** (1995) 2900
- [137] E. H. Oelkers and H. C. Helgeson, *J. Phys. Chem.* **92** (1988) 1631
- [138] L. Li and N. O. Egiebor, *Energy & Fuels* **8** (1994) 1126
- [139] Y. Matsumura, T. Nunoura, T. Urase and K. Yamamoto, *J. Hazard. Mater. B* **73** (2000) 245
- [140] M. Goto, T. Nada, S. Kawajiri, A. Kodama and T. Hirose, *J. Chem. Eng. Jpn.* **30** (1997) 813
- [141] S. H. Lin, S. J. Ho and C. L. Wu, *Ind. Eng. Chem. Res.* **35** (1996) 307
- [142] J. Haber, in *Perspectives in Catalysis*, J. M. Thomas, and K. I. Zamaraev (Eds.), Blackwell Scientific Publications, Oxford, 1992
- [143] P. A. Giguère and I. D. Liu, *Can. J. Chem.* **35** (1957) 283
- [144] J. Takagi and K. Ishigure, *Nucl. Sci. Eng.* **89** (1985) 177
- [145] E. Croiset, S. F. Rice and R. G. Hanush, *AIChE J.* **43** (1997) 2343
- [146] D. A. House, *Chem. Rev.* **62** (1962) 185
- [147] W. K. Wilmarth and A. Haim, in *Peroxide Reaction Mechanisms*, J. O. Edwards (Ed.) Interscience Publishers, New York, 1962, p. 175
- [148] R. G. R. Bacon, R. Grime and D. J. Munro, *J. Chem. Soc.* (1954) 2275
- [149] S. K. Gupta and S. C. Saksena, *J. Indian Chem. Soc.* **64** (1987) 154
- [150] M. A. Salem and A. H. Gemeay, *Monatsh. Chem.* **131** (2000) 117
- [151] R. F. Wilson, *Limnol. Oceanogr.* **6** (1961) 259
- [152] D. W. Menzel and R. F. Vaccaro, *Limnol. Oceanogr.* **9** (1964) 138
- [153] B. J. Kim, S. Qi and R. S. Shanley, *Water Environ. Res.* **66** (1994) 440
- [154] R. J. Ayen, *JOM*, May (1994), 30
- [155] *Hazardous Waste Remediation, Innovative Treatment Technologies*, H. M. Freeman and E. F. Harris (Eds.), Technomic Publishing Company, Inc., Lancaster (PA), USA, 1995
- [156] M. U. Beer, P. J. Wood and J. Weisz, *Cereal Chem.* **74** (1997) 476
- [157] S. B. Hawthorne, Y. Yang and D. J. Miller, *Anal. Chem.* **66** (1994) 2912
- [158] S. B. Hawthorne, C. B. Grabanski, E. Martin and D. J. Miller, *J. Chromatogr. A* **892** (2000) 421
- [159] A. J. M. Lagadec, D. J. Miller, A. V. Lilke and S. B. Hawthorne, *Environ. Sci. Technol.* **34** (2000) 1542
- [160] Y. Yang, S. B. Hawthorne and D. J. Miller, *Environ. Sci. Technol.* **31** (1997) 430
- [161] K. Hartonen, G. Meissner, T. Kesälä and M-L. Riekkola, *J. Microcolumn Sep.* **12** (2000) 412
- [162] Y. Yang, S. Bøwadt, S. B. Hawthorne and D. J. Miller, *Anal. Chem.* **67** (1995) 4571

- [163] S. B. Hawthorne, C. B. Grabanski, K. J. Hageman and D. J. Miller, *J. Chromatogr. A* **814** (1998) 151
- [164] B. van Bavel, K. Hartonen., C. Rappe, L. Öberg and M-L. Riekkola, *Organohalogen Compd.* **40** (1999) 577
- [165] B. van Bavel, K. Hartonen., C. Rappe and M-L. Riekkola, *Analyst* **124** (1999) 1351
- [166] M. M. Jiménez-Carmona, J. J. Manclús, A. Montoya and M. D. Luque de Castro, *J. Chromatogr.* **785** (1997) 329
- [167] A. E. McGowin, K. K. Adom and A. K. Obubuafo, *Chemosphere*, **45** (2001) 857
- [168] R. S. Ayala and M. D. Luque de Castro, *Food Chem.* **75** (2001) 109-113
- [169] M. M. Jiménez-Carmona and M. D. Luque de Castro, *Chromatogr.*, **50** (1999) 578
- [170] A. Basile, M. M. Jiménez-Carmona and A. A. Clifford, *J. Agric. Food Chem.* **46** (1998) 5205
- [171] S. Rovio, K. Hartonen, Y. Holm, R. Hiltunen and M.-L. Riekkola, *Flavour Fragr. J.* **14** (1999) 399
- [172] H. Daimon and J. Pawliszy, *Anal. Commun.* **33** (1996) 421
- [173] K. J. Hageman, L. Mazeas, C. B. Grabanski, D. J. Miller and S. B. Hawthorne, *Anal. Chem.* **68** (1996) 3892
- [174] T. Hyötyläinen, T. Andersson, K. Hartonen, K. Kuosmanen and M.-L- Riekkola, *Anal. Chem.* **72** (2000) 3070
- [175] H. Luik and L. Luik, *Energy Sources* **23** (2001) 449
- [176] J. Yanik, M. Yueksel, M. Saglam, N. Olukcu, K. Bartle and B. Frere, *Fuel* **74** (1995) 46
- [177] I. Windal, S. Hawthorne and E. de Pauw, *Organohal. Comp.* **40** (1999) 591
- [178] S. M. Walas, *Chemical Reaction Engineering Handbook of Solved Problems*, Gordon and Breach Publishers, USA, 1995, p. 36
- [179] D. Goulden and D. H. J. Anthony, *Anal. Chem.* **50** (1978) 953
- [180] K. Hatakeda, Y. Ikushima, O. Sato, T. Aizawa and N. Saito, *Chem. Eng. Sci.* **54** (1999) 3079
- [181] S.T. Kolaczowski, F. J. Beltran, D. B. McLurgh and F. J. Rivas, *TransIChemE* **75** (1997) 257
- [182] S. B. Hawthorne and C. B. Grabanski, *Environ. Sci. Technol.* **34** (2000) 4348
- [183] G. D. Sayles, C. M. Acheson, M. J. Kupferle, Y. Shan, Q. Zhou, J. R. Meier, L. Chang and R. C. Brenner, *Environ. Sci. Technol.* **33** (1999) 4310
- [184] G. Cornelissen, H. Rigterink, M. M. A. Ferdinandy and P. C. M. van Noort, *Environ. Sci. Technol.* **32** (1998) 966
- [185] R. L. Holliday, B. Y. M. Jong and J. W. Kolis, *J. Supercrit. Fluids* **12** (1998) 255