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HAZARDOUS WASTE DISPOSAL BY SUPERCRITICAL FLUIDS

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ABSTRACT

In the presence of water or carbon dioxide in the supercritical state, organic materials can be oxidized by oxygen practically completely within seconds. The report contains descriptions of test rigs and experimental findings. Additional R&D work is necessary for technical-scale application in cleaning organically polluted liquid effluents.

INTRODUCTION

The supercritical state of a substance is reached when the temperature and the pressure exceed the critical point. For water, this is at Tc = 374°C and Pc = 221 bar, at a density of 0.32 g/cm3. Transition into the supercritical state of a substance is also characterized by drastic changes in its properties [see, e.g., 1]. The dielectric constant of water drops from approx. 80 to <10, and the transfer properties are improved because of the low, gas-like viscosity and the considerably higher diffusion coefficient. The modified properties of water are reflected, among other things, in its solvent power: organic substances become more soluble and, as a consequence, homogeneously miscible with other substances, while inorganic salts become largely insoluble and are precipitated. In carbon dioxide (Tc = 31.2°C, pc = 73 bar, ρc = 0.46 g/cm3), the physical

properties and the material characteristics change along the same lines as described above for water.

M. Modell suggested an application for supercritical water in 1982 [2 ,3], which has since been called Supercritical Water Oxidation (SCWO). This is the oxidation of organic matter to carbon dioxide and water by means of oxidants, such as oxygen, in the presence of supercritical water. Compared with oxidation reactions in subcritical water, e.g. under conditions of wet oxidation [4], the SCWO reaction was seen to proceed much faster and much more completely. Practically complete conversions were achieved within one minute. The explanation can be seen in homogeneous mixing of the reactants described above, in which transfer blocks due to phase boundaries are avoided.

The most extensive development work in scaling up SCWO to a commercially viable industrial process was conducted in the United States of America and is still being funded by the U.S. Department of Energy and other government agencies [5]. The state of the art of approx. 1990 with respect to SCWO can be summarized as follows [6]:

- At 250 bar and 500-600°C, all organic compounds under study are degraded more than 99% within some 10 seconds.
- Organically bound carbon is mainly converted into CO_2, and small amounts of CO; organically bound nitrogen gives rise to molecular nitrogen and small quantities of NH_3 and N_2O; no higher nitrogen oxides were found. Organically bound halogens give rise to the corresponding hydrohalic acids which, in turn, produce salts when neutralized with alkalies.
- If the duration of the reaction is shorter, the degradation of organic molecules, in part, ends with intermediate products, such as acetic acid and ketones.
- The presence of halogens gives rise to pronounced corrosive attack upon the reactor material, especially near the critical point.
- No satisfactory procedures have as yet been developed and demonstrated on a technical scale for handling the precipitated salts and solids in continuous-flow apparatuses to be operated over long periods of time.

In general, chances are considered quite positive of SCWO being applied on an industrial scale in waste management, including the disposal of warfare agents and nuclear materials necessary in the United States. After all, the procedure not only achieves a practically complete separation of organic substances but, at the same time, converts these substances into safe products, even some inorganic materials (NO_3-, NH_4+). In the gas phase, no further downstream purification is necessary except for occasional monitoring for carbon monoxide.

At the Karlsruhe Research Center, the decision was taken in the early nineties to participate in the further development of SCWO. The process was felt to offer a high application potential because of the high degree of product purity achieved, the high space - time yield , and the relatively low operating temperature which avoids the formation of higher nitrogen oxides; however, certain requirements in terms of materials and process technology must be met if these goals are to be reached. With a view to other purification techniques, suitable applications were seen in those cases where fast *in situ* disposal of organically polluted liquid effluents is necessary, e.g., in product lines in chemical industry. At the same time, the procedure was deemed capable of disposing of liquid effluent concentrates from separation processes which, so far, either had to be put into repositories or, traditionally, had been incinerated.

At the same time, work has been started in which carbon dioxide is used in a supercritical state, initially as an extracting agent for organic materials [7]. However, this is based also on the intention to study a combination of both procedures: pollutant removal and pollutant oxidation [8].

R&D work on SCWO is conducted also elsewhere in Germany, especially about the disposal of pharmaceutical waste [9], other kinds of industrial waste [10, 11], and contaminated soil [12]. Activities of the French CEA have become known, and also in Japan such programs are under development [13].

References in the literature so far indicate just one commercial plant using SCWO [14]. The plant is to have been commissioned in Austin, Texas, by the Texaco Chemical Company in 1994. The starting material is

a long-chained organic material processed together with amines; consequently, problems arising from halogen induced corrosion, and also salt formation, can probably be excluded.

EXPERIMENTAL

Our experimental studies of SCWO are conducted exclusively in continuous-flow equipment. Initially, following the model of the Massachusetts Institute of Technology, a facility with a throughput of approx. 1 kg of water/h was built. Other design objectives were a maximum pressure of 300 bar, a maximum ambient temperature of 580°C, and a minimum residence time in the reactor of a few seconds.

Figure 1 shows a basic design diagram of the plant. The reactor consists of a high-pressure resistant tube of 2.1-mm inner diameter and 6-m length. An electrically heated fluidized sand bed is positioned around the helical tube which, at the same time, acts as a thermostat. Three feed streams have been installed. The main stream is water or an aqueous solution of carbon dioxide. The secondary stream is an organic liquid. Both streams are moved by pumps. Then there is the gas supply, the compressor of which so far has been used only to feed air as the oxidant. After passing through preheaters, the media reach static mixers, then the reactor, then a cooler and, finally, the back-pressure regulator. The products are separated in a phase separator. In the liquid phase, the quantity and the TOC content (DC-90 carbon analyzer made by the Dohrmann company) and, if possible, also specific organic compounds are determined. In the gas phase, the volume flow is measured and the fractions of CO_2, CO, and O_2 are analyzed continuously (IR-photometer with oxygen probe: URAS 10 E made by Hartmann und Braun). Moreover, the mass flows (weighing and flowmeter, respectively) are measured on the input side; the temperature of the media and also the temperatures along the reactor tube are measured at up to 20 selected points; also,the systems pressure is measured.

Later, another continuous-flow experimental facility with a throughput of 10 kg of water/h was erected. The concept is largely identical with that used in the 1-kg plant, but there are major differences in

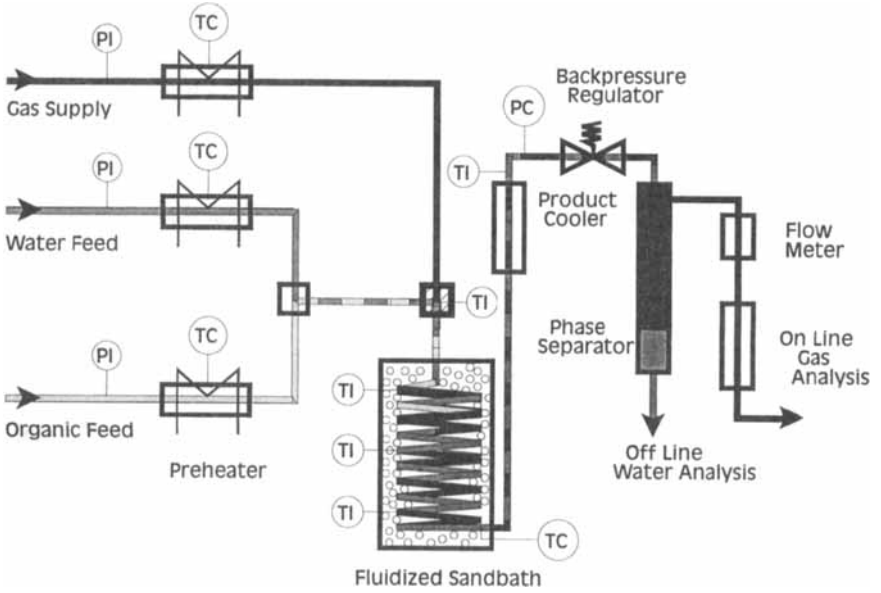

FIGURE 1. Flowsheet of the 1-kg SCWO facility.

points of detail, as is evident from Table 1. Figure 2 shows a simplified flowsheet of the facility. Fig. 3 is a photograph of the 15-m-long tubular reactor made of Inconel 625 with an inner diameter of 8 mm.

DATA ACQUISITION AND PROCESSING

The 1-kg facility at present has 33 temperature and 4 pressure measurement points, whose 4-20 mA signals, as well as the three analog outputs of the photometer, are digitized by I/O PAK modules (Action Instruments). Through the photoelectric barrier of a gas meter the gas flow generates pulses counted by an I/O PAK module. Current data of the measurement transducers are made available at a serial interface. Two digital balances (Sartorius) furnish the current weight of the aqueous and organic receiving tanks, also via one serial interface each. They are used to avoid uncertainties in direct measurements of small liquid flows.

TABLE 1. CHARACTERISTICS OF THE SCWO FACILITIES

Throughput	Approx.10 kg Water/h	Approx. 1 kg Water/h
Reactor geometry	8 mm dia. 15 m length	2.1 mm dia. 5.55 m length
Reactor material	Inconel 625	1.4401
Design pressure	400 bar	300 bar
Design temperature	600°C	580°C
Starting materials	Solutions, emulsions, air	Solutions, air
(planned)	(Suspensions) (Sludges) (Oxygen)	

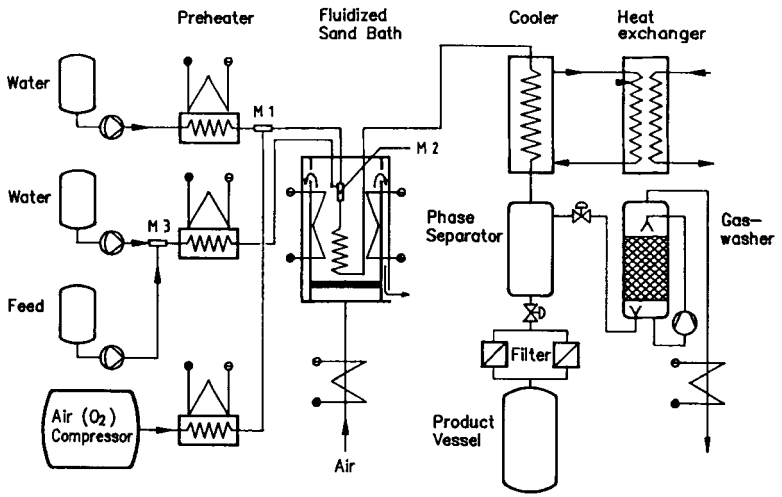

FIGURE 2. Simplified flowsheet of the 10-kg SCWO facility.

FIGURE 3. Tubular reactor of the 10-kg SCWO facility.

These are the standard functions of the data acquisition computer:

- Scanning all measured data through the three serial interfaces (RS232) at a rate of less than 1/s.
- Calculating streams of materials from noisy differences in masses and counts by means of suitable numerical filters.
- Graphic and numerical visualization of various data groups as a function of time and location, with alarm and switching functions.
- Controlling the heating power of preheaters and of the fluidized sand bed.
- Data filing.
- Subsequent fade-in of off-line data (analytical results).
- Remote observation and evaluation of the process by LAN and/or serial computer coupling, with remote control capacity in routine operation.

The programming interface VISCO [15, 16], originally developed in-house for modeling and simulation work, was for the first time used as instrumentation and control software, as the typical sequences of

events in simulation and data acquisition differ qualitatively only in their origins of data. In one case, it is the solutions of model equations; in the other case, it is the process data which must be visualized, analyzed, and documented. Any open experimental environment must provide the indispensable facilities for asynchronous interventions and modifications, perhaps even while the system is in operation, and for freely programmable sequence algorithms (such as extrapolation, decision trees, fuzzy algebra). The drivers, which can be configured in the VISCO interpreter part, can easily be used to operate, under MS-DOS, up to four serial interfaces of any communication protocol without the need to extend the hardware. In this way, integrated control, computer coupling, data visualization, filing, and evaluation up to on-line modeling and on-line process simulation are possible.

One difficulty is posed by controlling the operating temperature of the reactor. While the preheaters were easily controlled by a conventional PID algorithm, this approach failed when applied to the temperature of the fluidized sand bed. The fluidized sand bed used for thermostating exhibits complex control behavior because of the inhomogeneous, temperature-dependent fluidization and also because of its relatively large mass; this is further aggravated by exothermal reactions with short time constants. Only the use of a fuzzy controller turned out to be a satisfactory and directly usable solution.

In the 10-kg facility, the differences relative to the 1-kg facility are not only the larger number of measuring stations but, in particular, the safety-related measurement and switching points demanded and acceptance-tested by the Technical Inspectorate (TÜV) which, in principle, must be independent of any other data acquisition system. As a storage programmed control system (Siemens Simatic) was used, the data acquisition computer did not have to exercise any control duties but merely allow their parametrization. The other functions are similar to those of the laboratory-scale plant. Warning and switching signals are indicated by a satellite PC serially coupled to the acquisition PC. The controllers, as well as the warning and the switching stations, are parametrized by means of a graphic tablet underlying the process flowsheet or, in a conventional way, by means of keyboards. As in the 1-kg facility,

the measured data are held in interim storage on one local and one network data ring buffer each for reasons of data security, and are always available to an unlimited number of observation stations.

RESULTS OF OXIDATION IN SUPERCRITICAL WATER

One fundamental example studied was the oxidation of ethanol in the 1-kg facility. The basic experimental data are summarized in Table 2.

Under the experimental conditions selected, a steady-state equilibrium was established after only some 10 minutes. The temperature sensors distributed over the length of the tubular reactor showed readings higher than the thermostat temperature only over the first meter. The maximum measured was 650°C at a distance of only 5 cm from the entry of the reactor. In the liquid product, TOC levels of 0.8% were recorded relative to the starting material. The gaseous product contained 10.3/2.0/3.4 parts by volume of $CO_2/CO/O_2$. In other words, most of the degradation of ethanol had occurred within one second and had been completed approx. 99% after four seconds. The oxidation product was CO_2 and, at a rate of 2.0 vol.% of the offgas, also CO. The oxygen had not been consumed entirely.

In consecutive experiments, the modifications were studied which were necessary to reduce the peak temperature, increase conversion, and reduce CO generation. Factors varied were the throughput of the organic substance, the throughput of air and, hence, also that of the excess oxidant, the residence time of the reaction mix in the reactor (mainly by varying the throughputs of water), and the thermostat temperature. The results of these tentative studies led to a selection of test conditions under which SCWO was studied in greater detail with ethanol, n-hexane, cyclohexane, benzene, toluene, and nitrobenzene as the model substances. Important quantitative findings are shown in Fig. 4 to 11.

Results obtained in the oxidation of ethanol are shown in Fig. 4 [17]. 30 g of ethanol and 430 std. l of air were fed throughout, which means twice the stoichiometric volume of oxygen as the oxidant relative to

TABLE 2. BASIC EXPERIMENTAL DATA

Pressure	240 ± 10 bar
Thermostat	540 ± 5°C
Feed	860 ± 20 g water/h 60 ± 3 g ethanol/h 430 ± 2 std. l air/h
Oxidant volume	Simple stoichiometry for the production of $CO_2 + H_2O$
Volume flow at 540°C	Approx. 18 l/h
Flow rate at 540°C	Approx. 1.4 m/s

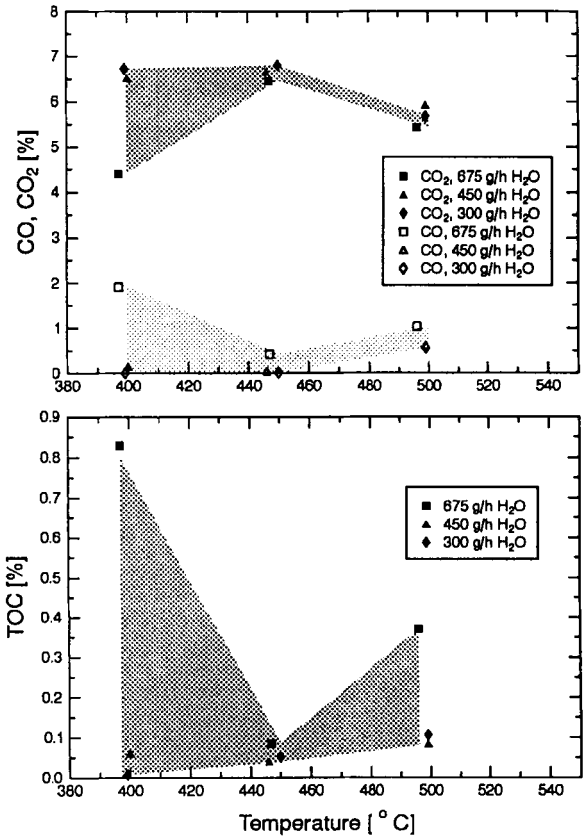

FIGURE 4. CO, CO_2, and TOC results in the oxidation of ethanol in the 1-kg facility as a function of the thermostat temperature and the water throughput.

CO_2. Factors varied were the water throughput (300-675 g/h) and the thermostat temperature (400-500°C). The TOC levels measured in the liquid phase of the product (throughout all the diagrams below) are referred to the TOC content of the starting product and, after subtraction from 100%, used as an indicator of conversion. The maximum conversion was 99.98% and was achieved at 400°C thermostat temperature and a water throughput of 300 g/h. As the thermostat temperature and the water throughput, respectively, increased, conversion dropped to 99.2%. Traces of acetone were detected qualitatively. The reduction in TOC levels in the liquid product phase was paralleled in the gas phase by the measured decrease of CO from approx. 1 to <0.02 vol.%.

Only recently, the SCWO of ethanol was conducted also in the 10-kg facility. 10 kg of water, 200 g of ethanol, and 2.9, 5.8, and 8.7, respectively, std. m^3 of air were supplied per hour, which is tantamount to 2, 4, and 6 times, respectively, the amount of oxidant. In addition, the thermostat temperature was varied between 400 and 550°C. Comparing the results (Fig. 5) with those obtained in the 1-kg facility indicates that conversions are in agreement, while their temperature dependence differs. In the 10-kg facility, conversion rises with the temperature. Further experiments will have to be conducted to explain the differences.

The results obtained in the oxidation of n-hexane in the 1-kg facility are shown in Fig. 6. In these experiments, 1.2 times the stoichiometric quantity of the oxidant was used. The maximum conversion was 99.5% and was attained at 540°C thermostat temperature. The TOC level in the liquid product phase, and the CO fraction in the gas phase rose with decreasing thermostat temperature. Also increased water flows resulted in more incomplete oxidation. Traces of phenol and polyaromatic compounds were identified in the liquid product phase.

The results of the oxidation of cyclohexane at 550°C are summarized in Fig. 7. Conversion rates were always above 96%, even reaching a maximum of 99.98%. The organic substances remaining in the liquid product phase were examined in greater detail than before. Traces were identified of some 30 aliphatic compounds (branched alkanes, alkenes, and aldehydes) and a similar number of even more highly con-

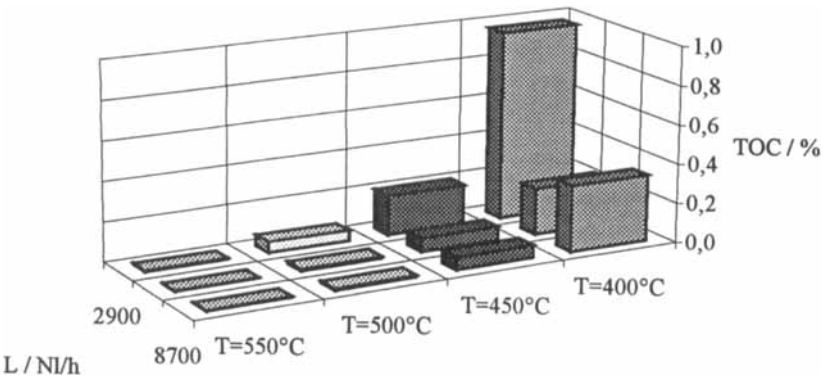

FIGURE 5. TOC results in the oxidation of ethanol in the 10-kg facility as a function of the thermostat temperature, T, and the air throughput, L.

densed aromatic compounds (naphthalene, anthracene, fluorene, pyrene). In the gas phase, 0.2 vol.% CO was found for maximum conversion. The results did not indicate any clearcut influences of the parameters varied.

The oxidation of benzene so far has been conducted only at 550°C thermostat temperature. At lower temperatures, the equipment plugged up after some 20 minutes, probably due to pyrolysis reactions. Figure 8 shows the TOC levels in the liquid product phase. The highest conversions were found at the longest residence times in each case, the maximum being 99.7%. One striking feature was the reduction in conversion to some 90% as a function of shorter residence times; this finding was less pronounced with the other model substances under the same conditions; it consequently agrees with the special stability of the unsubstituted aromatic nucleus.

Toluene exhibited an oxidation behavior similar to that of n-hexane. In the 1-kg facility, a maximum conversion of 99.5% was obtained when 2.7 times the stoichiometric amount of oxygen (860 std. l of air and 30 g of toluene per hour), a thermostat temperature of 540°C, and a water throughput of 900 g/h were used. When the last two parameters were

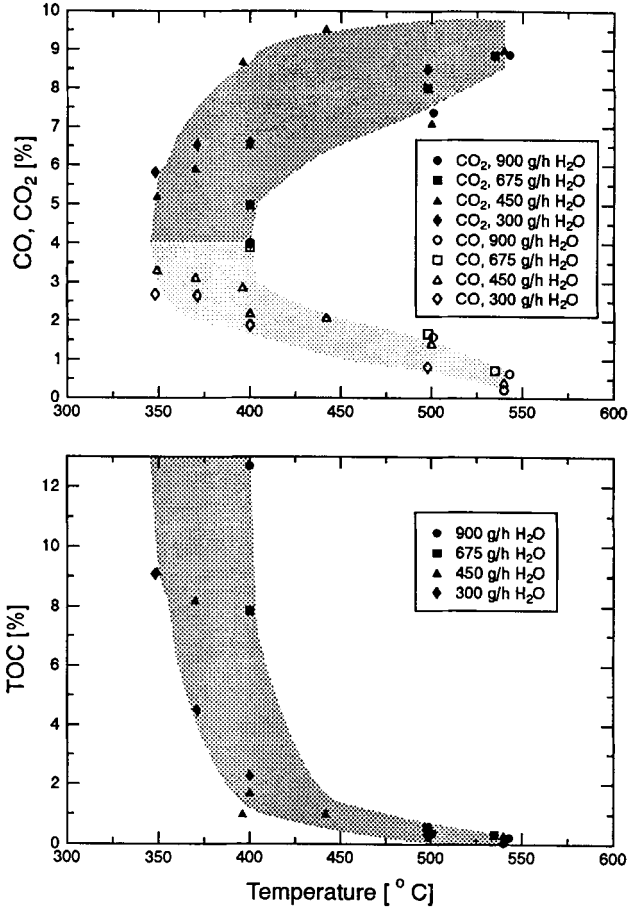

FIGURE 6. CO, CO_2, and TOC results in the oxidation of n-hexane as a function of the thermostat temperature and the water throughput.

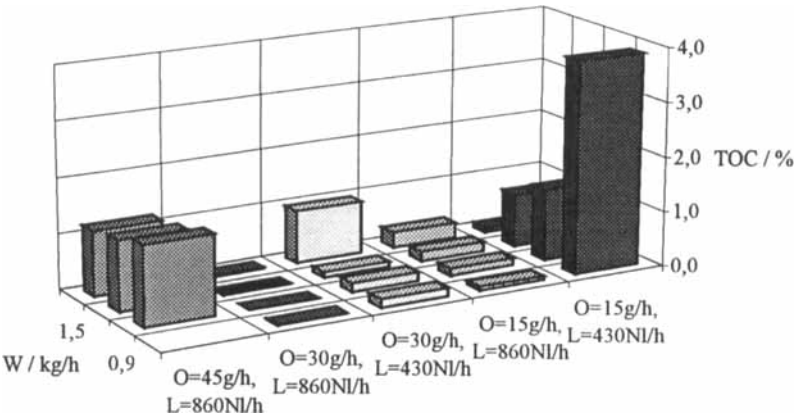

FIGURE 7. TOC results in the oxidation of cyclohexane at 550°C as a function of the throughputs of water, W; air, L; and cyclohexane, O.

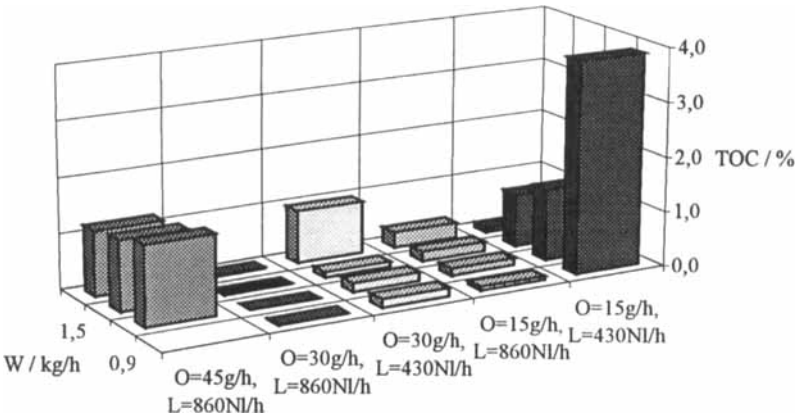

FIGURE 8. TOC results in the oxidation of benzene at 550°C as a function of the throughputs of water, W; air, L; and benzene, O.

lower, the liquid product phase exhibited rising TOC levels as well as yellowing; also, traces of polyaromatic compounds were found.

Experiments in the 10-kg facility produced a similar finding (Fig. 9). In this case, 10 kg of water, 300 g of toluene, and 4.3, 8.7, and 13 std. m^3 of air, respectively, were fed per hour, which means 1.35, 2.7, and 4.1, respectively, times the stoichiometric volume of the oxidant. The residence time in the reactor was between 10 and 15 seconds. Above 500°C, all conversions exceeded 99.9%, while they clearly dropped to 97-98% below this temperature.

Figure 10 shows the temperature profile over the first meter of the tubular reactor in the 1-kg facility as a function of the thermostat temperature and the water throughput. As the water throughput rose, the maximum temperature of a profile decreased. At the same time, the location of the peak temperature moved into downstream sectors of the reactor. This latter phenomenon was more pronounced at higher thermostat temperatures.

Finally, the oxidation of nitrobenzene was studied. Again, at 500°C thermostat temperature, continuous flow was upset, as in the case of benzene. The experiments at 550°C had the same residence times, but higher excess oxidant volumes than in the case of benzene. Conversion rates >99% were achieved throughout, the highest one at the longest residence times. Figure 11 is a summary of the findings.

After experiments with model substances, also some preliminary experiments with industrial types of liquid effluent were conducted in the 10-kg facility. The liquid effluent used consisted of sludge from municipal sewage treatment and liquid effluents from the paper industry. The findings confirmed that the simple tubular reactor is able, in principle, to treat such waste with low salt and corrosive chlorine contents. This is not true of higher salinities, as was borne out by experiments with liquid effluents from a pharmaceutical company. The alkaline solution (pH = 12.5) contained 6.5 g of sulfate and 3.3 g of chloride per liter; the whole dry residue amounted to 5%, the TOC share to 2%. Table 3 shows the experimental conditions and the results.

The results must be evaluated in the light of the fact that the experiments were conducted only for 30/40 and 120 minutes, respectively. In

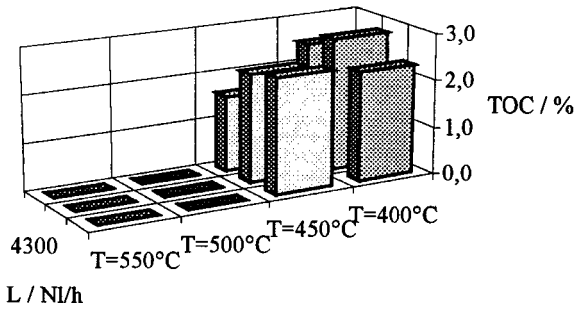

FIGURE 9. TOC results in the oxidation of toluene in the 10-kg facility as a function of the thermostat temperature, T, and the throughput of air, L.

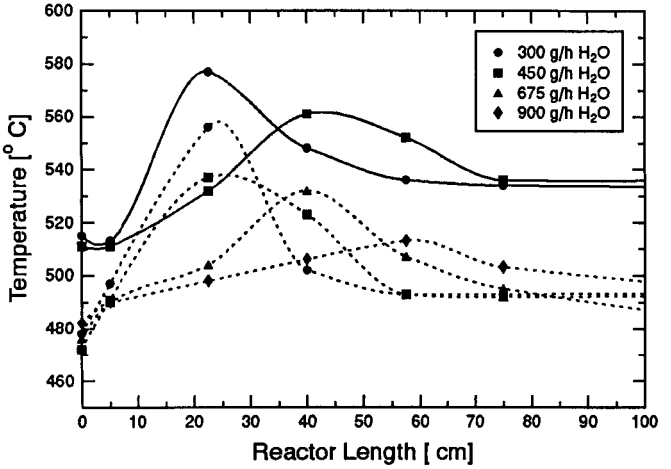

FIGURE 10. Temperature profile over the first meter of the tubular reactor in the oxidation of toluene as a function of the thermostat temperature and the water throughput.

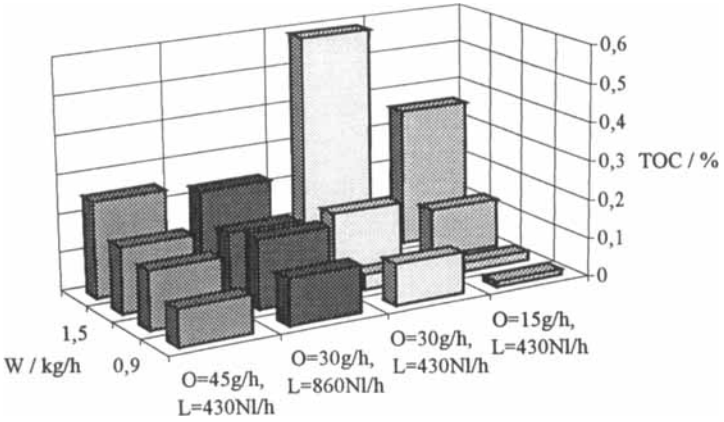

FIGURE 11. TOC results in the oxidation of nitrobenzene at 550°C as a function of the throughputs of water, W; air, L; and nitrobenzene, O.

TABLE 3. CONDITIONS AND FINDINGS OF THE OXIDATION OF PHARMACEUTICAL LIQUID EFFLUENT
(A) ONLY RELATIVE TO CARBON
(B) RELATIVE TO THE TOC INLET LEVEL

		Experiment 1	Experiment 2	Experiment 3
Thermostat temperature		550°C	550°C	410°C
Reactor residence time		50 s	25 s	30 s
Excess oxidant	(a)	20 fold	9 fold	9 fold
Residual TOC	(b)	3%	11%	17%
Conversion		97%	89%	83%

Experiments 1 and 2, the duration was limited by plugging, as was to be expected, because the solubility of salts in water is greatly reduced at a thermostat temperature of 550°C. Probably, the equilibrium between the starting materials and the products had not yet been reached, and the conversion rates therefore should be taken only as tentative values. On the other hand, the findings obtained in Experiment 3 at only 410°C are considered realistic with respect to the chemical conversion, as this experiment was characterized by a continuous flow. The precipitation of salts was controlled by measurements of electric conductivity and showed constant levels in the product which were only slightly below those in the starting material.

The outcome of the preliminary experiments conducted to remove the organic components from pharmaceutical liquid effluent shows that the problem of salt precipitation cannot be managed in a simple tubular reactor. Consequently, efforts will be intensified at the Karlsruhe Research Center to solve the problem by a suitable reactor concept. The current favored design is that of an unpressurized inner tube resistant to corrosion, which would avoid firmly adhering salt precipitates.

RESULTS OF OXIDATION IN SUPERCRITICAL CARBON DIOXIDE

Carbon dioxide in a supercritical condition is used as an extractant more and more frequently [18]. Applications are also under preparation in waste management, e.g., for removing oil from grits and grinds in metal working [19, 20]. In case the organic substances separated in this way cannot be recycled, they must be disposed of. If they are toxic, they should be converted into harmless substances. Oxidation to carbon dioxide and water would be an appropriate way. At this point the question should be raised whether the oxidation of organic materials is feasible not only in the presence of supercritical water, but also in supercritical carbon dioxide as the reactant. In that case, direct coupling of the separation and destruction of pollutants, e.g., from aqueous solutions, would be possible.

In an attempt to answer this question, some preliminary experiments were carried out with ethanol and toluene as model substances; 35 g of

the organic material and 350 g of carbon dioxide were fed per hour, plus 1.5 times the stoichiometric quantity of oxygen in air as the oxidant. Again, 240 bar pressure was applied. The thermostat temperature was varied.

Figure 12 shows the operating diagram of a 6-hour experiment in which the thermostat temperature was raised from an initial 350°C to 370°C, then reduced continuously to 270°C and then raised again to 350°C (upper section). In the bottom section of the diagram, the O_2 and CO volume fractions, respectively, in the product gas as well as the TOC levels in the product liquid are plotted over the starting material. The drop in the oxygen curve characterized the onset of oxidation; at the same time, measurable quantities of CO, on the average 0.1 vol.%, were found. The TOC levels determined in the batch mode quickly reached a level of approx. 0.01%, which corresponds to a conversion >99.99%. While the temperature was being reduced, the CO levels were seen to rise. When 275°C had been reached, the gas fractions dropped back to their initial levels, and oxidation had come to a standstill. It was resumed when the thermostat temperature exceeded 335°C. In the temperature profile of the reactor (Fig. 13), a narrow peak was measured at 50 cm with 580°C as the maximum level, which is 230°C above the thermostat temperature. As the thermostat temperature dropped, the temperature peak moved on and, at the same time, the maximum level decreased.

The experiments with toluene produced the same result qualitatively, but with these quantitative differences: Oxidation did not start until a thermostat temperature of 350°C, and ceased at 290°C. Major fluctuations were found in the oxygen content of the product gas; the CO fraction averaged 0.5 vol.%. The TOC levels in the product liquid amounted to 0.1%. However, the samples were turbid, which is indicative of finely dispersed solids possibly caused by pyrolysis.

In summary, the preliminary experiments conducted in carbon dioxide indicated that ethanol and toluene can be oxidized by air practically completely at 240 bar within a matter of seconds. Unlike the case of water, the ambient temperature of the reactor must only be

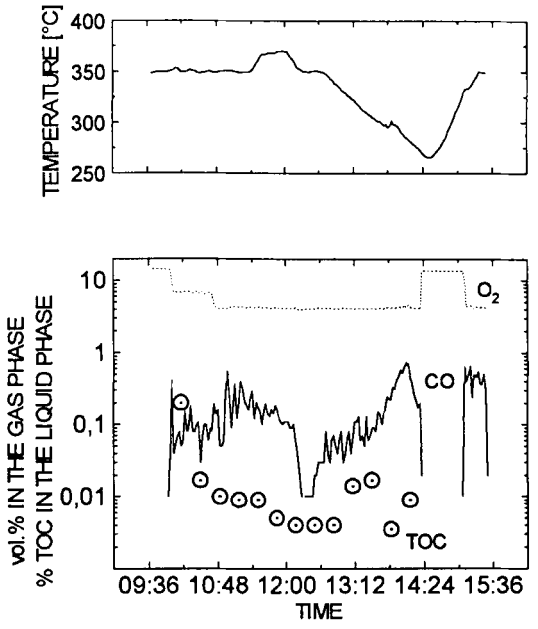

FIGURE 12. Operating diagram of the O_2, CO, and TOC measurements in the oxidation of ethanol in carbon dioxide as a function of the thermostat temperature.

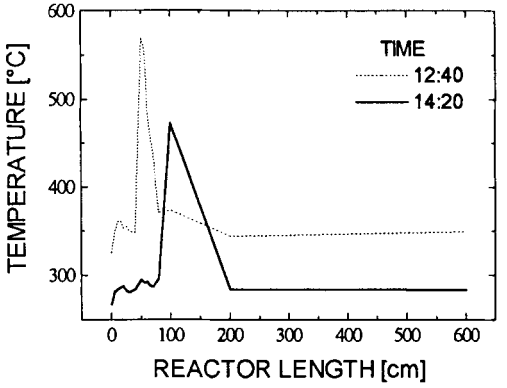

FIGURE 13. Temperature profile over the tubular reactor in the oxidation of ethanol in carbon dioxide as a function of the thermostat temperature.

approx. 300°C. Pyrolysis products seem to be generated at higher temperatures.

After this fundamental clarification,more detailed studies seem to be indicated. These should include the conditions under which pyrolysis can be excluded; an identification of the traces of secondary products; the oxidizing capability of organic pollutants up to pollutant mixes. Should the positive findings be confirmed, the plan referred to initially, namely to use carbon dioxide as a common medium for the sequential removal and destruction of pollutants, would be put into effect on a technical scale.

RESULTS OF MATERIALS STUDIES

One of the main problems in SCWO technology is the corrosion of reactor materials. The oxidation of real waste is likely to have in the reaction mixture not only oxygen, but also chloride, sulfate, phosphate, fluoride, and other corrosive species. The combination of high temperature, pressure, density of the fluid, and concentration of the aggressive medium presents an enormous corrosive stress on all materials. In our studies, samples of high-pressure and high-temperature resistant tubes were used. The sample length was 500 mm, the outer diameter varied between 14.4 and 20 mm, and the inner diameter was 8 mm. The corrosion tests are conducted in two facilities specially built for the purpose. The tubular samples are heated electrically by a metal block in the central zone (200 mm).

While the metal samples are being investigated, experiments are conducted under the same conditions with ceramic substances introduced as small specimen solids. Chloride is the most important corrosive ion in SCWO. In our study, it is being simulated by hydrochloric acid. In the first series of tests, the time planned was 150 hours; the maximum temperature, 450°C; and the rated pressure, 240 bar.

The first alloys to be tested were Inconel 625, Hastelloy C-276, Nicrofer 6025, Nicrofer 5923, and Haynes Alloy 214. For comparison, the austenitic CrNi stainless steel type No. 1.4401 and an Inconel 625 tube gold plated on the inside were studied under the same conditions.

In the experiments, initially only with oxygen (up to 5 mol/kg), it was seen that all Ni-base alloys exhibited slight corrosion under the typical experimental conditions. Corrosion became more pronounced when 1800 ppm HCl had been added to the water. 1.4401 type stainless steel showed pronounced general corrosion up to 0.6 mm in the temperature transition zones of the reactor. Inconel 625 showed less pronounced general corrosion. In both cases, a yellow-greenish precipitate consisting mainly of Ni, Cr, Cl, and O was found in the supercritical part of the tube.

In the experiments with oxygen (0.5 mol/kg) and hydrochloric acid (0,05 mol/kg) simultaneously present in the solution, fast corrosion was observed throughout. In all the materials tested, general corrosion was localized in the tube sections right upstream and downstream of the heating block.

An increase in HCl concentration to 0,5 mol/kg caused a dramatic acceleration in corrosion. As can be seen from Table 4, all experiments were stopped after a few hours.

In the tube section a short distance upstream and downstream of the metal heating block, Nicrofer 6025 and Haynes Alloy 214 exhibited pronounced corrosion. Figure 14 shows a cross-section through the sample of Haynes 214 after the experiment with 18,000 ppm HCl. The wall thickness was removed to approx. 1 mm, and the sample developed a leakage after one day of the experiment.

Metallographic examination of Inconel 625 showed a corrosive stress-induced crack in the tube section at a temperature close to 300°C. Figure 15 is a plot of all measurements of the wall thickness as a function of the tube position for various experiments with Inconel 625. These data are typical of all the other alloys and demonstrate the more rapid corrosion in the temperature range close to the critical point [21].

The findings made so far can be summarized as follows: All Ni-base alloys tested exhibit fast corrosion in acid solutions containing oxygen and chloride under conditions typical of SCWO. As there is often also stress corrosion cracking, it is not possible to indicate times to rupture for an SCWO reactor made of these materials.

TABLE 4. CORROSION OF NI-BASE ALLOYS BY [HCL] = 0,5 MOL/KG.
SCC = STRESS CORROSION CRACKING;
TC = TRANSGRANULAR CORROSION;
IC = INTERGRANULAR CORROSION.

Material	Time to leakage/plugging	Maximum corrosion depth (mm)	Type of defect
Inconel 625	46 h (L)	1	SCC, TC, IC
Haynes 214	22 h (L)	2.6	IC
Hastelloy C-276	60 h (V)	1	IC
Nicrofer 5923	19 h (L)	1	IC
Nicrofer 6025	32 h (L)	4.8	-

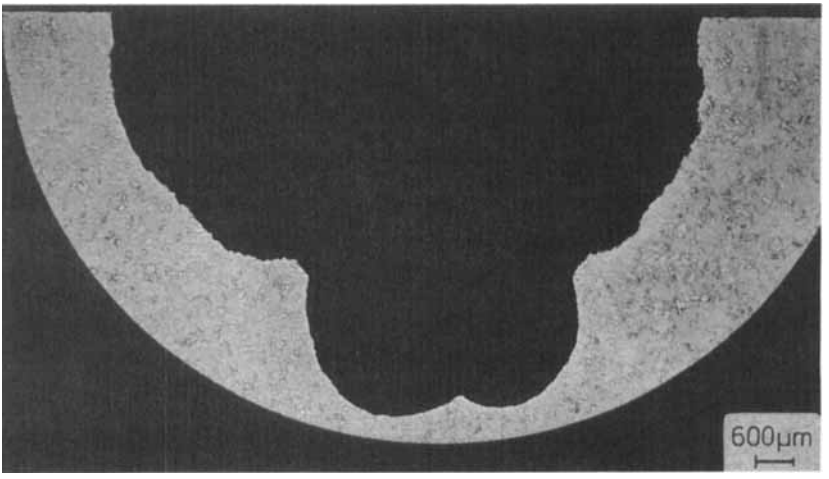

FIGURE 14. Haynes Alloy 214 sample at the point of leakage.

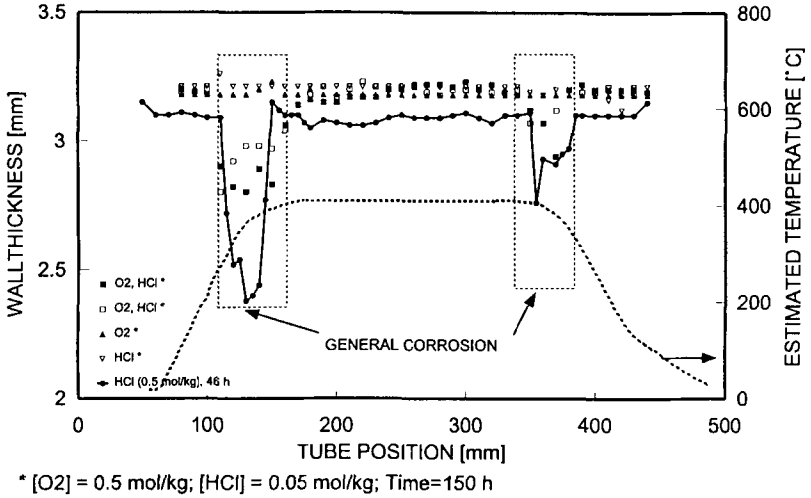

FIGURE 15. Corrosion of Inconel 625 in supercritical water.

In the first experiment with an Inconel 625 tube gold plated on the inside, no improvement in corrosion resistance was observed. Under the experimental conditions chosen, corrosion occurs most quickly in the temperature range about the critical point. This finding helps to localize corrosion problems in technical-scale plants. In a reactor for oxidative degradation of toxic wastes in supercritical water, the most pronounced corrosion problem is expected in the area of the cooler.

Among various ceramic substances, oxide ceramics exhibited the best corrosion resistance under conditions typical of SCWO [22].

In addition to work performed at the Karlsruhe Research Center, materials studies are being conducted also elsewhere [23-26]. One of the ideas being pursued is the possibility to increase reactor service life greatly by means of titanium or platinum linings of the wall.

CONCLUSION AND ACKNOWLEDGEMENT

Real liquid effluents polluted with organic substances, as a rule, also contain salts. As indicated in the report, their handling in SCWO reac-

tors, next to the restriction of corrosion, is one of the key problems in connection with the application of this technique on an industrial scale. Consequently, more suitable reactors must be developed, which is an activity pursued also by other groups [27-30].

An alternative solution to the problem is seen in the concept of first removing organic substances from liquid effluents and oxidizing them later. Supercritical carbon dioxide can be used for removal, while water, and probably also carbon dioxide, in the supercritical condition can be employed for oxidation. Carbon dioxide would allow the removal and oxidation steps to be coupled, which we feel is an attractive proposition. Our future activities will also be directed at this dual use of carbon dioxide.

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