

Effect of the Temperature of Water on the Degradation of Methylene Blue by the Generation of Radio Frequency Plasma in Water

Ippei Miyamoto¹, Tsunehiro Maehara¹, Hiroshi Miyaoka¹,
Shingo Onishi¹, Shinobu Mukasa¹, Hiromichi Toyota¹,
Makoto Kuramoto², Shinfuku Nomura¹ and Ayato Kawashima³

¹Graduate School of Science and Engineering, Ehime University, Matsuyama 790-8577, Japan

²Integrated Center for Science, Ehime University, Matsuyama 790-8577, Japan

³Faculty of Agriculture, Ehime University, Matsuyama 790-8566, Japan

(Received: 1 September 2008 / Accepted: 24 January 2009)

We produced and maintained radio frequency (RF) plasma in water at atmospheric pressure under two temperature ranges (30 °C and 70 °C), in order to investigate the effect of the temperature of water on the amount of RF plasma generated. The results of the spectroscopic measurement show that the generation of an OH radical is almost independent of the temperature of water, although the size of the bubbles surrounding the RF plasma clearly depends on it. A larger amount of methylene blue is degraded and a smaller amount of hydrogen peroxide is generated at 70 °C than those degraded and generated at 30 °C.

Keywords: RF plasma, in water, degradation, methylene blue, temperature of water, hydrogen peroxide, Fenton's reaction

1. Introduction

Discharge in water is one of the most important phenomena that is responsible for the formation of advanced oxidation processes (AOPs). A number of studies have been conducted on pulsed streamer corona discharges generated in water [1–4].

Recently, the generation of radio frequency (RF) plasma has been reported [5,6]. RF power is injected into water through an electrode. RF plasma surrounded by bubbles is generated and maintained on the electrode. According to ref [5], RF plasmas are used for the degradation of methylene blue dissolved in water. This degradation may be caused by the generation of an OH radical produced by RF plasma. In ref [6], the formation of hydrogen peroxide was also reported. Hydrogen peroxide is produced through the recombination processes of radicals in water or in the bubbles that surround the RF plasma. Gradual degradation of methylene blue after being exposed to RF plasma was observed. OH radical and hydrogen peroxide play an important role in the decomposition of pollutants. The behavior of such active species depends on the temperature of water. The size of the bubble surrounding the RF plasma may also depend on the temperature of water. Therefore, the degradation of methylene blue may also depend on the temperature of water. However, in ref [6], the temperature of water was fixed at approximately 60–80 °C. In this paper, in order to discuss the effect of the temperature of water on

the formation of RF plasma in water, we produced and maintained RF plasma at a high and low temperature range (30 °C and 70 °C) and compared them. For comparison, the formation of spectral lines, the generation of hydrogen peroxide and the degradation of methylene blue were observed. In addition, rapid degradation of methylene blue was realized via Fenton's reaction.

2. Experimental Apparatus

RF plasma was generated in water between two electrodes placed in a vessel (Fig. 1). A Pyrex glass container (ID: 80 mm, height: 90 mm) was used as the vessel. During degradation experiments, 300 mL of methylene blue solution was stored in this container. Water flowing through a copper pipe was used to control the temperature of water. Since the copper pipe was connected to the ground line, it functioned as a counter electrode. The temperature of water was measured using a fiber optic thermometer (FL-2000, Anritsu Meter); this thermometer can measure the temperature of water without being affected by the interference caused by an electromagnetic oscillation, because it employs the dependence of reflection of light by luminophor upon temperature. The temperature of water was controlled within ± 2 °C.

The lower electrode was a tungsten rod, its diameter and length were 2.8 mm, 20 mm, respectively. It was covered with a ceramic pipe (OD: 5 mm, ID: 3 mm).

The electrodes were connected to a resonator by copper leads, and RF power was supplied to the resonator through the tuner from a power supply (T161-6013H, Thamway, $f = 13.56$ MHz). Here, the net input power was fixed at 210 W.

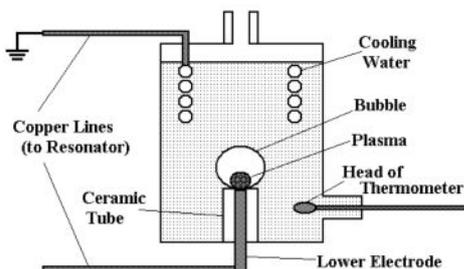


Fig. 1 Experimental setup

We employed two spectroscopic measurement systems. The first system was equipped with a USB 2000 spectrometer (Ocean Optics). In this system, the measured spectrum was in the range of 300–800 nm. The top of the optical fiber, used for performing spectroscopic measurement, was placed beside the Pyrex glass container and was not connected to the focal lens. The second system was equipped with a double-beam spectrophotometer (U-2810, Hitachi). This system was used to measure the absorbance spectra of the methylene blue solution.

3. Experimental Results

Typical RF plasma generated in water at an atmospheric pressure is shown in Fig. 2. As shown in Figs. 2 (a) and (b), the temperatures of water, T_{water} , were 30 °C and 70 °C. The images were shown in these captured figures using a CCD camera (Digicam, Panasonic) through an ND filter. In both the cases, the size of the RF plasma is estimated to be $\phi 3$ mm in comparison with that of the ceramic pipe (OD: 5 mm). These plasmas were surrounded by bubbles, and they were stable when RF power was supplied (15 min). Although the sizes of the RF plasmas were almost the same, size of the bubbles were clearly different. While the size of the bubble was $\phi 6$ mm at $T_{\text{water}} = 30$ °C, it had a width of 15 mm and a height of 7 mm at $T_{\text{water}} = 70$ °C.

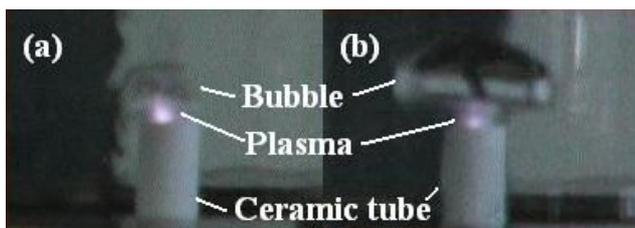


Fig. 2 Image of RF plasma generated in water. The temperatures of the water are maintained at (a) $T_{\text{water}} = 30$ °C and (b) 70 °C.

After the position of the experimental set up was fixed for comparing the spectral lines generated at $T_{\text{water}} = 30$ °C and 70 °C, spectroscopic measurements were performed. Emission spectra of RF plasma generated in water are shown in Fig. 3. In Figs. 3(a) and (b), $T_{\text{water}} = 30$ °C and 70 °C, respectively. The spectral lines, generated due to the radicals, OH, O, and H, were observed. This shows that water molecules are decomposed into OH, O, and H radicals by the RF plasma. The emission spectra shown in Figs. 3 (a) and (b) are very similar. In particular, spectral lines generated due to OH had the same intensity. This suggests that the number and temperature of the OH radical is almost independent of the temperature of water.

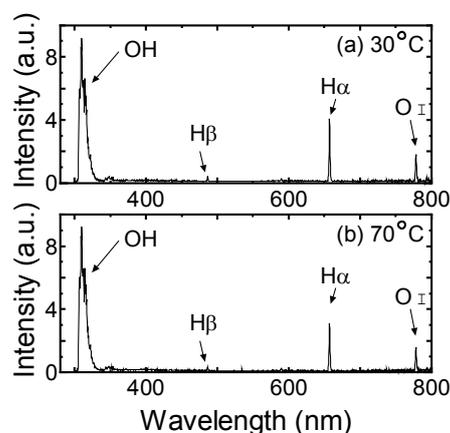


Fig. 3 Emission spectra of RF plasma generated in pure water. The temperatures of the water are maintained at (a) $T_{\text{water}} = 30$ °C and (b) 70 °C. Spectral data are accumulated for 1 s. The data of five samples are averaged.

RF plasma generated in water can degrade organic matter. Here, we used a methylene blue solution (5 mg/L, 300 mL). When this solution was exposed to RF plasma, its color lightened with respect to that of the solution before it was exposed to the RF plasma. This variation in color was apparent from the absorbance spectra. Typical variation in the absorbance spectra with exposure time is shown in Fig. 4. In Fig. 4(a) and (b), $T_{\text{water}} = 30$ °C and 70 °C, respectively.

After the solution was exposed to the RF plasma, it was observed that the absorbance of three spectral peaks (246 nm, 292 nm, and 664 nm) decreased monotonously over an exposure time of 15 min and at $T_{\text{water}} = 30$ °C and 70 °C, the absorbance at 664 nm reduced to 0.6 and 0.35, respectively. On the other hand, the absorbance around 200 nm increased monotonously over an exposure time of 15 min and at $T_{\text{water}} = 30$ °C and 70 °C, the absorbance at 190 nm increased to 1 and 0.55, respectively.

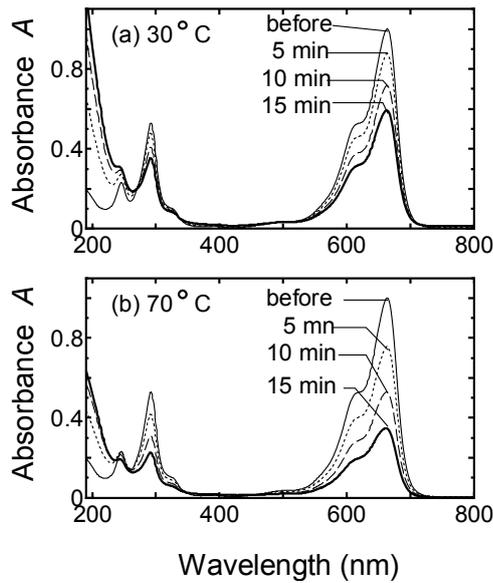


Fig. 4 Absorbance spectra of methylene blue solution before (solid line) and after exposure at (a) $T_{\text{water}} = 30\text{ }^{\circ}\text{C}$ and (b) $70\text{ }^{\circ}\text{C}$, respectively. The net input power is 210 W. Dotted, dashed, and bold lines correspond to the exposure time of 5, 10, and 15 min, respectively

As previously mentioned [6], hydrogen peroxide is also produced by the generation of RF plasma in water (Fig. 5). After pure water (300 mL) was exposed to RF plasma, the density of hydrogen peroxide was determined by using a hydrogen peroxide meter (PC compact, Aqualytic). In this meter, photometric detection during water analysis was carried out by measuring the concentration of hydrogen peroxide on the basis of the absorption of monochromatic light after the introduction of a reagent system. The reagent consists of N,N-diethyl-p-phenylenediamine sulfate (DPD). This detection method is termed “DPD method”. At $T_{\text{water}} = 30\text{ }^{\circ}\text{C}$, the density of hydrogen peroxide increased linearly with the exposure time. Over an exposure time of 15 min, the density of hydrogen peroxide reached 170 mg/L. At $T_{\text{water}} = 70\text{ }^{\circ}\text{C}$, the density saturated after 10 min at a constant value of approximately 70 mg/L. The density of hydrogen peroxide produced by the generation of RF plasma in water clearly depends on the temperature of water. This saturation suggests that at $T_{\text{water}} = 70\text{ }^{\circ}\text{C}$, hydrogen peroxide is decomposed over the same time as it is generated.

The amount of hydrogen peroxide generated was also measured at $T_{\text{water}} = 20\text{ }^{\circ}\text{C}$, which was the lowest temperature of water in the present system. The density of hydrogen peroxide at $T_{\text{water}} = 20\text{ }^{\circ}\text{C}$ was apparently higher than that at $T_{\text{water}} = 30\text{ }^{\circ}\text{C}$. Over the exposure time of 15 min, the density reached 188 mg/L. Energy density is calculated to be $900\text{ s} \times 210\text{ W}/300\text{ mL} = 630\text{ J/mL}$. Reference [7] shows that the density of hydrogen

peroxide generated by the pulsed streamer corona discharge (plus voltage: 19 kV) is approximately 100 mg/L at 630 J/mL.

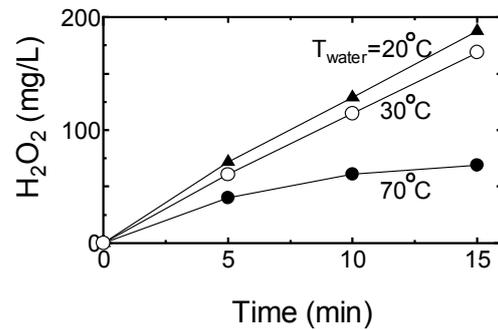


Fig5 Plot of the density of hydrogen peroxide against exposure time. Closed and open circles correspond to $T_{\text{water}} = 30\text{ }^{\circ}\text{C}$ and $70\text{ }^{\circ}\text{C}$, respectively.

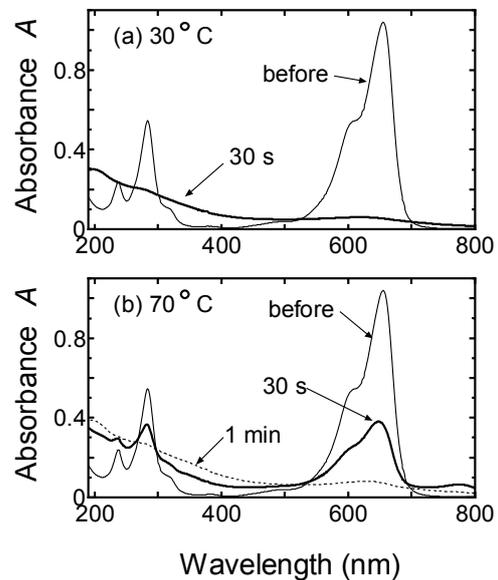


Fig. 6 Absorbance spectra of methylene blue solution before (solid line) and after being exposed to RF plasma with ferrous sulfate. The net input power is 210 W. Bold and dotted lines correspond to the exposure time of 30 and 60 s,

Rapid degradation can be achieved by the production of OH radical from hydrogen peroxide. Here, we regard Fenton’s reaction as one of the simplest method. It is well known that Fenton’s reaction is represented as



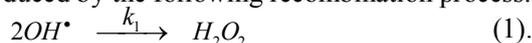
After ferrous sulfate (3 mg) was solved to methylene blue solution (300 mL, 5mg/L), it was exposed to RF plasma. The absorbance spectra of the methylene blue solution before and after being exposed to RF plasma are shown in Fig. 6. At $T_{\text{water}} = 30\text{ }^{\circ}\text{C}$, peaks in the absorbance spectra of methylene blue solution perfectly disappeared

over an exposure time of 30 s. This degradation is much faster comparing with that without ferrous sulfate (cf. Fig. 4). At $T_{\text{water}} = 70\text{ }^{\circ}\text{C}$, the peaks were visible over an exposure time of 30 s. Over an exposure time of 1 min, the peaks almost flattened. Therefore, the degradation rate at $T_{\text{water}} = 30\text{ }^{\circ}\text{C}$ is apparently higher than at $T_{\text{water}} = 70\text{ }^{\circ}\text{C}$. However, it is not clear whether this different degradation rate is essential or not. RF plasma is unstable for approximately 10 s after break down. The unstable plasma often leads to larger degradation than the stable plasma. Since the exposure time of 30 s is not large enough, we point out only the fact that rapid degradation can be achieved under both the cases of $T_{\text{water}}=30\text{ }^{\circ}\text{C}$ and $70\text{ }^{\circ}\text{C}$ at present.

4. Discussions

Figure 2 shows the different sizes of bubbles generated in water at each water temperature. The reason for the generation of bubbles with different size is explained as follows: RF plasmas are not in contact with water; however, they exist surrounded with vapor generated by the heat of the plasmas. Hereby, the plasmas appear as if these are generated in a bubble, as shown in Fig. 2. When the temperature of the water is lower than its saturation temperature, the vapor near the surface of the water is condenses. The lower the temperature of water, the higher is the condensation rate. Therefore, the size of the bubbles varies. Since we are investigating the dependence of the size of the bubbles on the temperature of water or RF power in detail, it will be published elsewhere in near future.

In order to discuss the effect of the temperature of water on the rate of decomposition of hydrogen peroxide, pure water was maintained at $70\text{ }^{\circ}\text{C}$ for 5 min without plasma. Here, hydrogen peroxide is produced by the generation of RF plasma in pure water. The densities of hydrogen peroxide before and after maintaining for 5 min were the same. This result suggests that the decomposition of hydrogen peroxide is not attributed to only high temperature of water but also to the existence of plasma. Hydrogen peroxide is produced by the following recombination process:

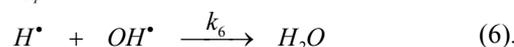
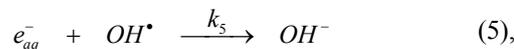


The reaction rate constant at $70\text{ }^{\circ}\text{C}$ is greater by 40% than that at $30\text{ }^{\circ}\text{C}$ (Table I). This implies a greater amount of hydrogen peroxide is produced at $70\text{ }^{\circ}\text{C}$ than $30\text{ }^{\circ}\text{C}$ when the number and temperature of OH radicals produced is almost independent of the temperature of water. The radicals and aqueous electrons generated in plasma decompose hydrogen peroxide by processes such as



The reaction rate constants of these reactions (k_2 , k_3 , and k_4) at $70\text{ }^{\circ}\text{C}$ are approximately twice those at $30\text{ }^{\circ}\text{C}$ (Table I); that is, an increase in the temperature of water results in a larger increase in the rate constants during the decomposition of hydrogen peroxide than that during the production of hydrogen peroxide. This result is qualitatively consistent with the fact that the density of hydrogen peroxide linearly increases at $30\text{ }^{\circ}\text{C}$ and it saturates at $70\text{ }^{\circ}\text{C}$, as shown in Fig. 5.

Although it is difficult to describe the decomposition of methylene blue on the basis of rate constants because of the complexity of the decomposition process, the OH radical may play a dominant role in the decomposition process due to its high oxidizing power. The OH radical is produced by reactions (3) and (4) in water as well as by decomposition of water in plasma; this radical is responsible for the decomposition of hydrogen peroxide at $70\text{ }^{\circ}\text{C}$, which in turn contributes to the decomposition of methylene blue. The OH radical is likely to decompose methylene blue at a high reaction rate in the high temperature range; these conditions are similar to those of other reactions. These results lead to enhancing the decomposition process. On the other hand, there are some processes that suppress the decomposition process, that is, the OH radical reacts with the aqueous electron or the H radical to form a stable molecule through the following reaction:



The rate constants of these reactions (k_5 and k_6) carried out at $70\text{ }^{\circ}\text{C}$ are larger by 40% than those at $30\text{ }^{\circ}\text{C}$ (Table I). Experimental results shown in Fig. 4 suggest that high water temperature significantly enhances the decomposition of methylene blue.

In Fig. 4, a reduction in the absorbance at 664 nm indicates that a high water temperature results in a high degradation rate. However, an increase in the absorbance at 190 nm with the exposure time at $T_{\text{water}} = 70\text{ }^{\circ}\text{C}$ is smaller than that at $T_{\text{water}} = 30\text{ }^{\circ}\text{C}$.

Table I Reaction rate constants [8]

	30 °C	70 °C
k_1 (L/mol s)	6.5×10^9	9.4×10^9
k_2 (L/mol s)	3.0×10^7	5.6×10^7
k_3 (L/mol s)	5.6×10^7	1.2×10^8
k_4 (L/mol s)	1.2×10^{10}	2.4×10^{10}
k_5 (L/mol s)	3.2×10^9	4.6×10^9
k_6 (L/mol s)	7.4×10^9	1.1×10^{10}

These results suggest that the increase in the absorbance at 190 nm is not attributed only to small molecules produced from methylene blue. Since it is suspected that the increase in absorbance at 190 nm with the exposure time attributed to hydrogen peroxide, the absorbance spectra of pure water exposed to RF plasma for 10 min at 210 W are measured. Absorbance was clearly observed below 300 nm, and it increased monotonously with a decrease in wavelength (Fig. 7(a)). At $T_{\text{water}} = 30\text{ }^{\circ}\text{C}$ and $70\text{ }^{\circ}\text{C}$, absorbance at 190 nm are 0.7 and 0.3, respectively. This suggests that the increase in absorbance at 190 nm may be attributed to the generation of hydrogen peroxide, is produced by RF plasma in the methylene blue solution as well as in pure water.

In Fig. 6, no absorbance peak is observed after an exposure time of 30 s at $T_{\text{water}} = 30\text{ }^{\circ}\text{C}$ or 1 min at $T_{\text{water}} = 70\text{ }^{\circ}\text{C}$. Only a flat spectrum is observed. In this spectrum, absorption due to Fe^{3+} is dominant. This interpretation is based on the fact that a similar spectrum is observed when pure water (300 mL) mixed with ferrous sulfate (3 mg) without methylene blue is exposed to RF plasma for 1.5 min at $T_{\text{water}} = 30\text{ }^{\circ}\text{C}$. This spectrum is plotted by bold line in Fig. 7(b). Since a sufficient amount of hydrogen peroxide was generated (approximately $350\text{ }\mu\text{mol}$), all Fe^{2+} ions were changed into Fe^{3+} . In other words the bold line shown in Fig. 7(b) represents the amount of Fe^{3+} ions produced. Solid line in Fig. 7(b) represents the absorbance spectra of methylene blue solution mixed with ferrous sulfate and exposed to RF plasma for 1.5 min at $T_{\text{water}} = 30\text{ }^{\circ}\text{C}$. The difference between the solid and bold lines corresponds to the byproducts made via decomposition process of methylene blue. The difference is also plotted as a dashed line in Fig. 7(b). We can see the small absorbance in all the ranges. This suggests that almost of methylene blue is decomposed.

4. Summary

We compared the generation of RF plasma in water at atmospheric pressure in the two temperature ranges ($30\text{ }^{\circ}\text{C}$ and $70\text{ }^{\circ}\text{C}$), in order to investigate the effect of the temperature of water on the amount of RF plasma generated. The size of bubbles surrounding the RF plasma clearly depends on the temperature of water. The results of the spectroscopic measurement show that the generation of an OH radical is almost independent of the temperature of water. A larger amount of methylene blue is degraded and a smaller amount of hydrogen peroxide is generated at $70\text{ }^{\circ}\text{C}$ than those degraded and generated at $30\text{ }^{\circ}\text{C}$. In both the cases ($30\text{ }^{\circ}\text{C}$ and $70\text{ }^{\circ}\text{C}$), the addition of ferrous sulfate enhanced the degradation rate of methylene blue.

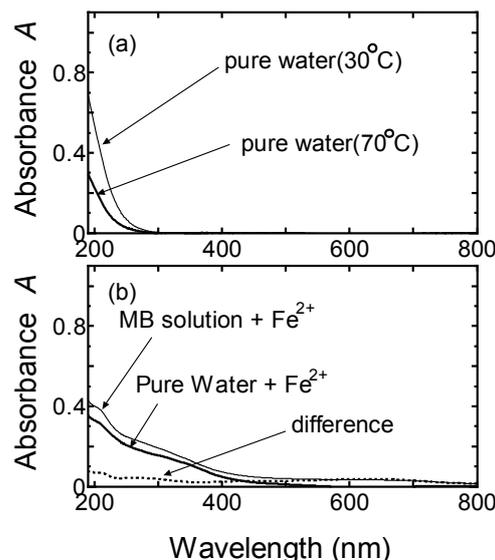


Fig. 7 (a) Absorbance spectra of pure water exposed to RF plasma for 10 min at $T_{\text{water}} = 30\text{ }^{\circ}\text{C}$ (solid line) and $T_{\text{water}} = 70\text{ }^{\circ}\text{C}$ (bold line). (b) Absorbance spectra of methylene blue solution (solid line) and pure water (bold line) with ferrous sulfate exposed to RF plasma for 1.5 min at $T_{\text{water}} = 30\text{ }^{\circ}\text{C}$. Dashed line shows the difference between the bold and solid lines.

Acknowledgements

The authors thank Mr. H. Okumura for his technical support.

References

- [1] J. S. Clements, M. Sato, R. H. Davis: IEEE Trans. Ind. Appl. **23** (1987) 224
- [2] A. K. Sharma, B. R. Locke, P. Arce, W. C. Finney: Hazard. Waste Hazard. Mater. **10** (1993) 209
- [3] A. A. Joshi, B. R. Lock, P. Arce, W. C. Finney: J. Hazard. Matter. **41** (1995) 3
- [4] D. R. Grymonpre, W. C. Finney, B. R. Locke: Chem Eng Sci **54** (1999) 3095
- [5] T. Maehara, H. Toyota, M. Kuramoto, *et al.*: Jpn. J. Appl. Phys. **45** (2006) 8864
- [6] T. Maehara, I. Miyamoto, *et al.*: Plasma Process. Plasma Chem. in Press.
- [7] M. Sato, T. Ohgiyama, J. S. Clements: IEEE Trans. Ind. Appl., **32** (1996) 106
- [8] A. J. Elliot: Radiat. Phys. Chem. **34** (1989) 753