



WET OXIDATION AS A PRETREATMENT METHOD FOR WASTEWATERS CONTAMINATED BY BIORESISTANT ORGANICS

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ABSTRACT

The partial wet air oxidation of aqueous solutions of polyethylene glycol, a model organic pollutant typically found in wastewaters of polymer-manufacturing, has been investigated at temperatures from 383 K to 513 K and oxygen partial pressures from 2 MPa to 3 MPa. The progress of the reaction was investigated in terms of COD and TOC removal, while fragmentation of the original polymer to lower molecular weight compounds was followed by means of liquid chromatography. The impact of various heterogeneous and homogeneous catalysts on the kinetics and mechanisms of the reaction has also been studied. Conversion of the model compound through various oxidation intermediates to end-products, such as carboxylic acids and oligomers, could be easily achieved even under mild operating conditions, while further total oxidation proved to be difficult even under more severe conditions. Catalysts were found to be, in general, capable of increasing the rates of total uncatalysed oxidation. The implications for complete removal of bioreistant organic pollutants by partial wet oxidation followed by a biological treatment step are also discussed. © 1997 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

Catalysts; kinetics; mechanisms; polyethylene glycol; wastewaters; wet oxidation.

INTRODUCTION

Many industrial, domestic and natural activities collectively result in the production of vast quantities of hazardous wastes of which wastewaters comprise as much as about 90% of these wastes. It was estimated (Tedder and Pohland, 1993) that, in 1989, the U.S. chemical industries alone generated nearly one billion metric tons of hazardous wastewaters which accounted for more than 99% of their annual waste production (including solid wastes and wastewaters). Given these large quantities for wastewater production, it is unsurprising that increasing environmental concerns have forced research towards the development of efficient wastewater treatment technologies.

The treatment and safe disposal of hazardous organic waste material in an environmentally acceptable manner and at a reasonable cost is a topic of great universal importance. There is little doubt that biological

processes will continue to be employed as a baseline treatment process for most organic wastewaters since they seem to fulfill the above two requirements.

However, the biological process does not always give satisfactory results, especially in the treatment of industrial wastewaters, because many organic substances produced by chemical and related industries are inhibitory, toxic or resistant to biological treatment. This is often due to the molecular structure of the molecules, which may preclude biological attack due to the size or the shape of the molecule and its associated functional groups.

On the other hand, complete mineralisation by chemical means may be far more expensive than biological treatment. Investment costs for biological processes may range from 5 to 20 times less than those of chemical processes such as ozonation or hydrogen peroxide oxidation, while treatment costs may range from 3 to 10 times less (Marco *et al.*, 1997). A comparison of wastewater treatment costs using wet air oxidation, incineration or sewer discharge treatment has been recently reported by Wigston (1995). To achieve 80% COD removal for a wastewater initially containing 50 g l^{-1} of COD, treatment costs would be as much as 100-120, 40-50 and 10.5 GBP t^{-1} for incineration, wet air oxidation and sewer discharge respectively.

Therefore, a potential and attractive alternative to complete oxidation through chemical means would be the use of a chemical oxidation pretreatment step to convert initially biorecalcitrant organics to more readily biodegradable intermediates, followed by biological oxidation of these intermediates to biogas, biomass and water (Scott and Ollis, 1995). This can be illustrated schematically as follows:



Wet air oxidation (WAO) provides an efficient method for either partial or total destruction of organic compounds such as phenol and substituted phenols, nitrogenous compounds and carboxylic acids (Mishra *et al.*, 1995) and is considered as a suitable wastewater treatment process for wastewaters with COD loads from 10 to 100 g l^{-1} , while incineration would be suitable for effluents having a COD greater than about 100 g l^{-1} and biological treatment would successfully treat non-toxic effluents with a COD of less than about 10 g l^{-1} (Debellefontaine *et al.*, 1996). Considerable attention has also been given to the catalytic wet oxidation using various heterogeneous and homogeneous catalysts since catalysts can potentially promote oxidation at shorter reaction times and milder operating conditions. A recent review of the catalytic wet oxidation has been published by Levec and Pintar (1995).

The purpose of this work is to investigate the partial wet air oxidation of polyethylene glycol, a model organic pollutant typically found in wastewaters of polymer manufacturing with respect to the rates of TOC and COD removal, reaction intermediates formed, as well as the impact of catalysts on the corresponding uncatalysed reaction. Implications for integrated chemical-biological treatment are also discussed.

MATERIALS AND METHODS

Choice of the model compound

Polyethylene glycols. Polyethylene glycols (PEG: $\text{OH}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$) are an important group of nonionic synthetic water-soluble polymers commonly used in the production of surfactants, lubricants, pharmaceuticals, antifreezes etc. Several studies have been performed on the biodegradability of various molecular weight (MW) PEGs (Haines and Alexander, 1975; Watson and Jones, 1976; Dwyer and Tiedje, 1986) and showed that although even high MW PEGs may be amenable to some extent of biodegradation, the rate of biodegradation substantially decreases with increasing MW, thus making high MW polymers practically non-biodegradable. Therefore, PEG of MW 10,000 has been chosen as a model polymer to be studied.

Catalysts

Heterogeneous catalysts Three metal oxide catalysts and two noble metal catalysts have been used in this study. (a) Metal oxides: (i) an iron oxide as FeO(OH) supplied by Aldrich Co., UK, (ii) a typical CuO.ZnO supported on Al₂O₃, as used for methanol synthesis, provided by ICI Katalco, UK in 5.6 mm pellets, (iii) a CuO.CoO.ZnO supported on Al₂O₃ (Cu/Zn:1.1/1, Cu/Co:6.2/1 molar ratio) supplied by Sd-Chemie AG, Germany. (b) Noble metals: platinum (Pt) and palladium (Pd), supplied by Aldrich Co., UK. In all these latter cases, the noble metal concentration was 0.5% w/w supported on alumina, and the catalysts were in the form of 3.2 mm pellets. The catalysts were crushed and sieved to produce particle sizes between 38-106 µm (used in slurry experiments), and were characterised with respect to their BET surface area by nitrogen adsorption. Comparison of relative catalytic activity between various catalysts used in slurry experiments was based on a common (BET surface area)/(liquid volume) ratio of about $2 \times 10^5 \text{ m}^2 \text{ m}^{-3}$.

Homogeneous catalyst Cu²⁺ ions in form of CuSO₄ were used as homogeneous catalyst. The appropriate amount of salt was dissolved in sulfuric acid and then mixed with the PEG solution to produce a concentration of 100 ppm of the metal ions.

Experimental and analytical

A 300 ml aqueous solution of PEG of initial concentration 1 g l⁻¹ was oxidised into a stainless steel high pressure autoclave (Baskerville Ltd, UK) capable of performing batch or continuous experiments at pressures up to 10 MPa and temperatures up to 573 K. In a typical (semibatch) run, the aqueous solution of the organic compound was loaded to the autoclave which was then pressurised with nitrogen to the desired pressure. The solution was sparged with nitrogen to remove any traces of oxygen present in the autoclave, and then heated up to the set temperature (under nitrogen) while stirring with a gas-inducing type impeller. Whenever a catalyst was used, it was introduced to the solution beforehand. As soon as the set temperature was achieved oxygen was continuously fed into the reactor at a flowrate of 1 l min⁻¹ to start the reaction. Experiments were carried out at temperatures from 383 K to 513 K and oxygen partial pressures from 2 MPa to 3 MPa.

Liquid samples of approximately 3 ml were periodically drawn from the reactor through a gas sparge tube located at the bottom of the reactor during a brief shut-off of the gas feed. They were collected into a sample cylinder which was directly connected to the gas line through a quick-connect coupling assembly, and immediately filtered to remove any catalyst particles present.

TOC was measured by combustion/non-dispersive infra red (NDIR) gas analysis with a Shimadzu 5050 TOC analyser. Total carbon was measured first followed by inorganic carbon and TOC was determined by subtracting inorganic carbon from total carbon. The relative standard deviation of three separate measurements was always less than 2%.

COD was determined by the dichromate method. The appropriate amount of sample was introduced into commercially available digestion solution (Hach Europe, Belgium) containing sulfuric acid, mercuric sulfate and chromic acid. The mixture was then incubated for 120 min at 423 K in a COD reactor (Model 45600-Hach Company, USA) and the COD concentration was measured colorimetrically using a DR/700 colorimeter (Camlab Ltd, UK). The average value of six separate readings was taken; the deviation never exceeded 3% for the range of COD concentrations measured.

Changes in molecular weight distribution during the oxidation of PEG were followed by means of gel permeation chromatography coupled with conventional HPLC. Polymers were separated on a PL Aquagel-OH 40, 300x7.5 mm column using pure water as the mobile phase at 1 ml min⁻¹. Detection was through a Shimadzu refractive index detector at high sensitivity range of 2×10^{-6} refractive index units. To determine the molecular weight corresponding to the chromatographic peaks, a calibration curve was established using standard calibration PEG samples. Short-chain organic acids formed during the oxidation were separated on a Hamilton PRP X-300, 7m, 250x4.1 mm column using 95:5 water (buffered with H₃PO₄):acetonitrile as an

isocratic mobile phase at 1 ml min^{-1} and detection was through a diode array detector at about 200 nm. The identity of the unknown compounds was determined by injecting standards of the suspected compounds and comparing their chromatograms to those of the unknown compounds with respect to peak retention times and spectral characteristics.

RESULTS AND DISCUSSION

Figures 1 and 2 show respectively the rates of TOC and COD removal during the uncatalysed oxidation of PEG at various temperatures.

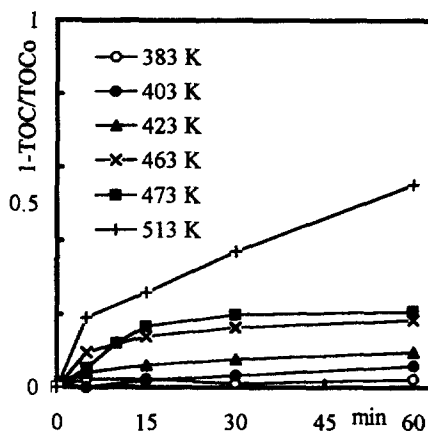


Figure 1. TOC removal during the uncatalysed oxidation at various temperatures.

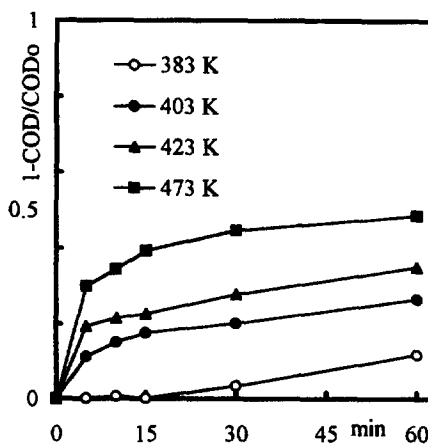


Figure 2. COD removal during the uncatalysed oxidation at various temperatures.

It can be seen that for temperatures from 383 K to 473 K, the rate of TOC removal is slow throughout the reaction, with only about 20% organics totally oxidised to carbon dioxide after 60 min at 473 K, while almost no total oxidation is observed after 60 min at 383 K- these results imply the presence in the reaction mixture of compounds which are resistant to total oxidation. Conversely, at 513 K the rate of TOC removal increases significantly and about 55% TOC reduction is achieved after 60 min. The rates of COD removal are higher than those of TOC removal with about 35% and 50% COD reduction being measured after 60 min of oxidation at 423 K and 473 K respectively. Figure 3 shows the MW distribution of PEG 10,000 after 5 and 30 min of oxidation respectively and five temperatures where the refractive index response is plotted

against the elution time from the chromatographic column. Peak A corresponds to the original PEG 10,000 while peak 1 corresponds to MW about 300 and peak 2 to ethylene glycol (MW=62). It can be seen that after 5 min at 383 K, some of the original PEG has been converted to lower MW fractions (see the broadening of the curve), while after 5 min at 423 K no PEG 10,000 is detected. Figure 3 also shows that only polymeric fractions of less than about 300 MW are present after 5 min at 463 K or 513 K. After 30 min of oxidation no PEG 10,000 is detected at any temperature above 383 K, while only at 383 K some of the original PEG still remains in the reaction mixture.

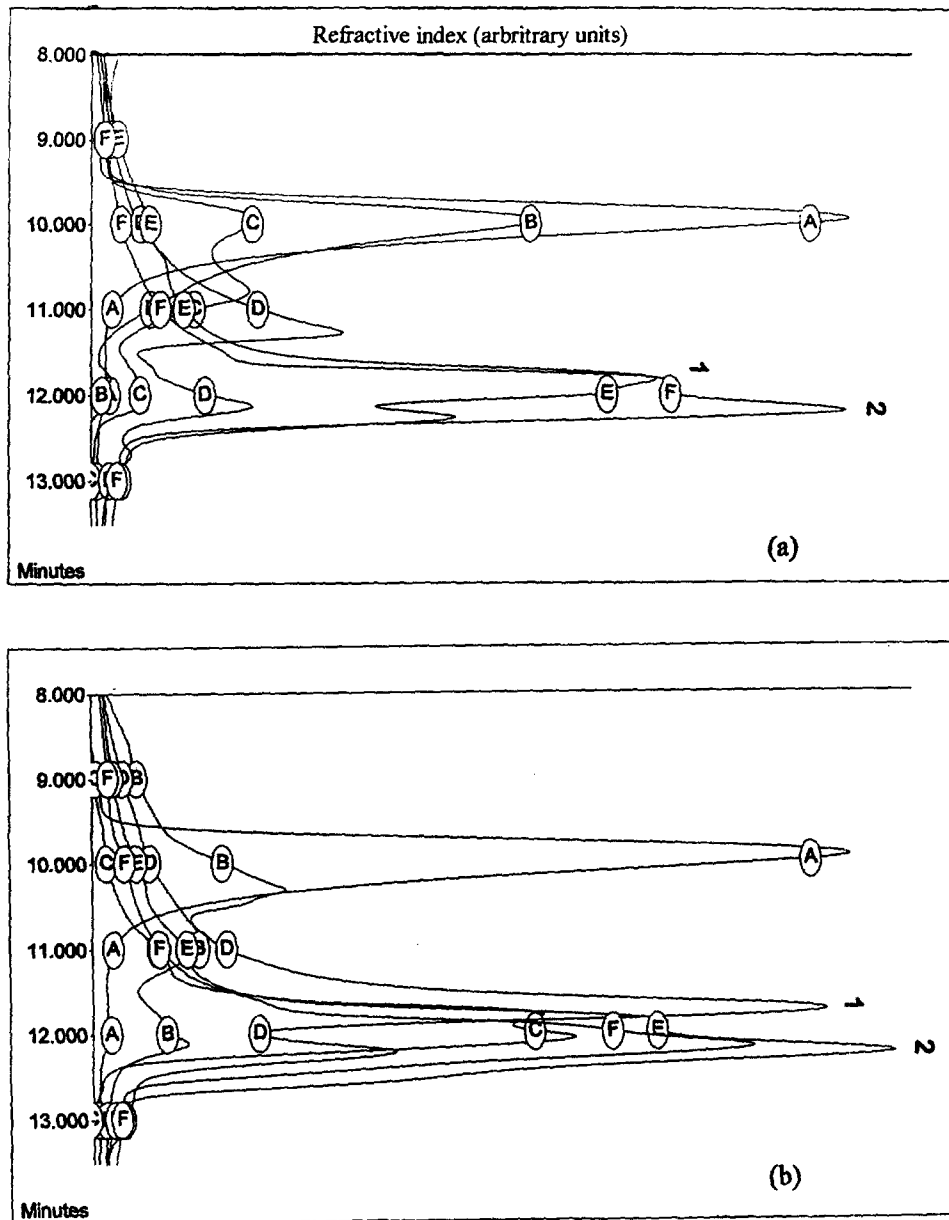


Figure 3. The MW distribution during the uncatalysed oxidation at various temperatures. (a) 5 min, (b) 30 min.
A: original PEG 10,000, B: 383 K, C: 403 K, D: 423 K, E: 463 K, F: 513 K.

These results show the ease with which the original PEG 10,000 can be broken down to its oligomeric fractions and possibly other non-polymeric compounds, which seem to be highly resistant to further oxidation, since little TOC removal has been observed at temperatures as high as 463 K.

In Figure 4, TOC is plotted against COD for various uncatalysed runs at temperatures from 383 K to 513 K and reaction times from 30 to 120 min. The horizontal dotted line corresponds to ideal partial oxidation (i.e. TOC would remain constant throughout the reaction, while COD would decrease), while the diagonal dotted line corresponds to ideal total oxidation (i.e. COD would decrease linearly with TOC). It can be seen that at temperatures up to 403 K (-x-) and reaction times up to 120 min, partial oxidation seems to dominate over total oxidation since a COD decrease is accompanied by little TOC removal. At temperatures from 423 K to 485 K (-O-) and reaction times from 30 to 120 min both partial and total oxidation become important, while only under severe conditions (i.e. 513 K and 120 min of oxidation, far left point --), total oxidation seems to dominate over partial oxidation.

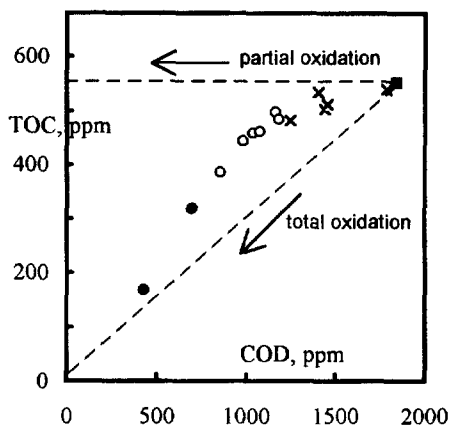


Figure 4. TOC versus COD during the uncatalysed oxidation at various temperatures.

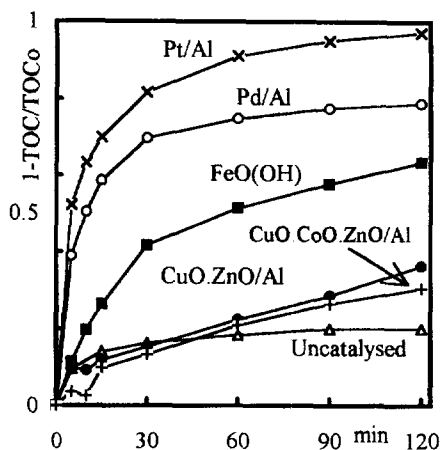


Figure 5. TOC removal during the catalysed oxidation at 463 K.

Figure 5 shows the rate of TOC removal during the oxidation of PEG at 463 K with five different catalysts in slurry. 80% and 97 % TOC removal was achieved after 30 min and 120 min of oxidation respectively using the Pt/Al catalyst while less than 20% TOC removal was observed during the uncatalysed run after 120 min. The Pd/Al catalyst resulted in almost 80% TOC removal after 120 min of oxidation. The metal oxide catalysts give rates of TOC removal which are significantly lower than those of the noble metal catalysts. FeO(OH) is of moderate activity, while CuO.ZnO/Al and CuO.CoO.ZnO/Al give rates of TOC removal which are comparable to that of the uncatalysed reaction. Figure 6 shows the rate of TOC removal with the Pt/Al catalyst at various temperatures. It can be seen that at temperatures as low as 403 K or 423 K, the catalyst can significantly increase the rate of the corresponding uncatalysed total oxidation-after 60 min of catalysed oxidation at 403 K more than 30% TOC removal was observed, while only about 5% TOC removal was observed during the corresponding uncatalysed reaction.

Figure 7 shows the rates of COD and TOC removal during the oxidation of PEG at various temperatures with homogeneous copper ions. It can be seen that the catalyst resulted in higher rates of both COD and TOC removal than those of the corresponding uncatalysed reaction. Although homogeneous copper catalyst seems to be more effective (in terms of TOC removal) than the corresponding copper-containing heterogeneous catalysts used in this study, its activity is still significantly lower than that of the noble metal catalysts used.

These results show that the formation of intermediates which are resistant to total oxidation (especially during the uncatalysed runs) accompany the fast removal of the original PEG. HPLC analysis showed the formation of lower organic acids such as acetic, oxalic and formic acid, as well as ethylene glycol accumulated in the reaction mixture and seemed to be strongly resistant to further oxidation.

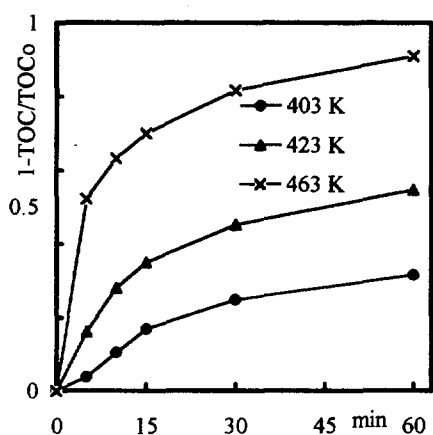


Figure 6. TOC removal during the catalysed oxidation with Pt/Al.

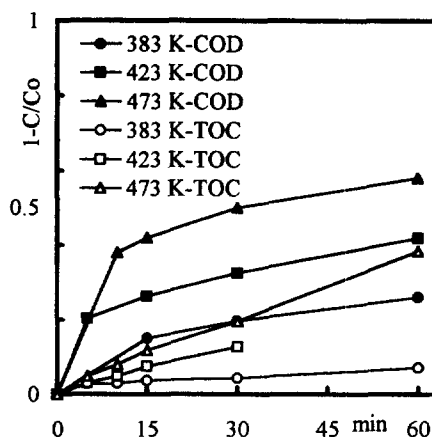
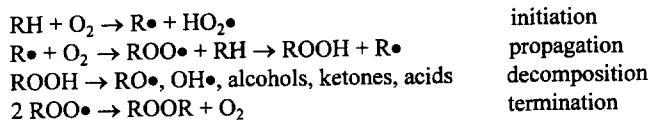
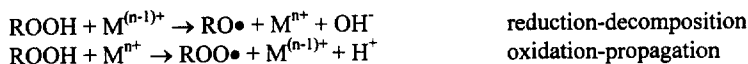


Figure 7. TOC and COD removal during the catalysed oxidation with Cu^{+2} .

The rapid oxidation of the original polymer and its transformation to lower MW fractions and organic acids can be explained through a free radical chain autoxidation mechanism. The depolymerisation occurs through the formation of alkyl radicals, alkyl peroxy radicals and hydroperoxides with the latter being responsible for an autocatalytic decomposition of the original polymer. The sequence of reactions occurring can be described, in general, as follows:



Catalysts may promote both the decomposition and the propagation steps by introducing redox reactions of the hydroperoxides:



Although the catalysts used in this study were found, in general, capable of enhancing the rates of total oxidation (i.e. TOC removal) by destroying compounds (such as carboxylic acids and oligomers) which are known to be refractory to total oxidation, depolymerisation of the original polymer to lower molecular weight compounds was found to be nearly as fast as that of the uncatalysed reaction. Therefore in the context of an integrated wet oxidation/biological wastewater treatment process where the role of the wet oxidation pretreatment will be the fragmentation of the original high molecular weight, bioresistant polymers to lower molecular weight, more readily biodegradable compounds rather than the complete mineralisation of the effluent, catalysts (even though offering improved TOC and COD removal rates) may actually be detrimental to the efficacy of the subsequent biological step. Taking also into account potential drawbacks associated with the use of catalysts, such as catalyst stability and deactivation, toxicity of leached metals, need of additional process steps to recycle or remove the catalysts, their use should be critically examined.

CONCLUSIONS

Polyethylene glycols are an important class of synthetic polymers whose widespread use causes environmental concerns related to the disposal and treatment of polymer-containing wastewaters. Although biodegradation of even high molecular weight PEGs is possible, it is commonly accepted that the effectiveness of biological treatment decreases with the molecular weight of polymer. An integrated chemical-biological process, using wet air oxidation as a pretreatment step, could provide an attractive alternative to conventional biological treatment. In this light, the wet oxidation of PEG 10,000 was studied in this work. It was found that the autocatalytic mechanism of thermochemical autoxidation is capable of converting macromolecules to lower molecular weight end products at very short reaction times and mild operating conditions. Oxidation for 15 min at 423 K can completely convert PEG 10,000 to lower molecular weight molecules which are mainly oligomers and carboxylic acids. Further oxidation of these intermediates to carbon dioxide proved to be difficult since compounds such as ethylene glycol and acetic acid are very resistant to chemical oxidation even under more severe conditions. Although catalysts (particularly heterogeneous noble metals) were found capable of increasing the rates of the uncatalysed total oxidation, they did not improve the rate of depolymerisation of the original polymer to lower molecular weight compounds.

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