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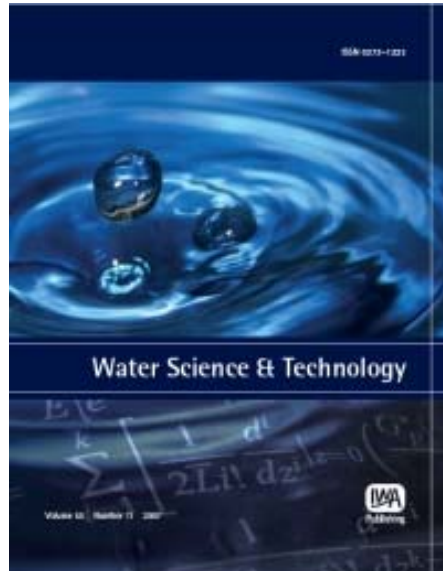


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Hydrolysis of polydimethylsiloxane fluids in controlled aqueous solutions

Gaëlle Ducom, Baptiste Laubie, Aurélie Ohannessian, Claire Chottier, Patrick Germain and Vincent Chatain

ABSTRACT

Accelerated degradation tests were performed on polydimethylsiloxane (PDMS) fluids in aqueous solutions and in extreme chemical conditions (pH 2–4 and 9–12). Results confirmed that silicones can be degraded by hydrolysis. Higher degradation levels were achieved in very acidic and alkaline conditions. Degradation products are probably polar siloxanols. In alkaline conditions, the counterion was found to have a strong influence on degradation level. Degradation kinetic studies (46 days) were also performed at different pH values. Supposing zeroth-order kinetics, degradation rate constants at 24 °C were estimated to 0.28 mgSi L⁻¹ day⁻¹ in NaOH solution (pH 12), 0.07 mgSi L⁻¹ day⁻¹ in HCl solution (pH 2) and 0.002 mgSi L⁻¹ day⁻¹ in demineralised water (pH 6). From these results, the following hypothesis was drawn: PDMS hydrolysis could occur in wastewater treatment plants and in landfill cells. It may be a first step in the formation of volatile organic silicon compounds (VOSiCs, including siloxanes) in biogas: coupled to biodegradation and (self-) condensation of degradation products, it could finally lead to VOSiCs.

Key words | degradation kinetics, hydrolysis, landfill, polydimethylsiloxane, wastewater

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INTRODUCTION

Silicones are widely used in consumer and industrial products because they present interesting properties such as thermal and chemical stability, low flammability, low surface tension and water repelling properties (Buch & Ingebrigtsen 1979). Silicone is a generic term to describe a class of polymeric compounds. They consist of an alternating silicon-oxygen backbone with organic substituents bonded to silicon. Substituent nature strongly influences polymer final properties. Thousands of different kinds of silicones are commercialised. Silicones can be classified as fluids, elastomers or resins depending on their molecular weight, the extent of cross-linking, and the type and number of organic groups bonded to the silicon atoms. Worldwide production has reached several million tons per year (Oku *et al.* 2002). In 2006, European production was 480,000 tons (CES 2008). This represents a silicone consumption around 1 kg per inhabitant per year in Western Europe and North America (Ohannessian 2008).

This study focusses on silicone fluids, representing more than 50% of silicones. In Europe, silicone fluids are mainly used in the following applications: processing aids, textile

applications, cosmetics, toiletries and medical/pharmaceutical preparations, papercoatings and defoamers (mainly backing for self-adhesives), paints, coatings and waxes, mechanical fluids (hydraulic fluids and lubricants/greases) (Lassen *et al.* 2005). Polydimethylsiloxanes (PDMSs) are the most widely used silicone fluids. Due to their intensive production, PDMSs can be found in all environmental compartments: sediments, soils, water, air, etc. (Fendinger *et al.* 1997; Graiver *et al.* 2003).

Two studies tried to assess the fate of organosilicon materials (including fluids) as a function of disposal mode. The first one (Allen *et al.* 1997) concerned the environmental loadings of industrial organosilicon materials for the USA in 1993. The material was apportioned into five environmental entry modes: air, wastewater treatment plants (WWTPs), soil, landfilled/incinerated/recycled, and dispersed (in more than one compartment). It was estimated that PDMS mainly ended up in WWTPs (26%), and landfill/incineration/recycling (48%). The second study (Ohannessian 2008) concerned the fate of organosilicon materials in 2007 in France. It was estimated that silicone fluids mainly

ended up in WWTPs (38%), landfills (30%) and incineration plants (26%).

It is commonly admitted that most volatile organic silicon compounds (VOSiCs, including siloxanes) in biogas result from silicones and/or their degradation products present in landfills and WWTPs (Schweigkofler & Niessner 1999; Dewil *et al.* 2006), but degradation of silicones was not demonstrated. Yet, this is of particular interest since VOSiCs are the main compounds penalising biogas-to-energy conversion, in gas engines for instance (Dewil *et al.* 2006; Ohannessian *et al.* 2008).

In a previous paper (Ohannessian *et al.* 2008), it was shown that biological degradation of PDMS might occur. In the present study, it was planned to demonstrate at laboratory-scale that PDMS chemical hydrolysis is also likely to occur. As PDMS degradation in the environment was of interest (WWTP and landfill), only hydrolysis was studied (in aqueous matrix). Extreme pHs (acidic or alkaline) were used in order to accelerate chemical degradation. The influence of pH was pointed out. Moreover, a kinetic study was performed (for 6 weeks) on PDMS degradation in aqueous solutions.

MATERIAL AND METHODS

Batch degradation tests were performed at laboratory scale under controlled chemical conditions. The tests were carried out in the dark (no photodegradation could occur). The materials used for all experiments were organosilicon

free. These precautions were adopted to prevent possible pollution due to silicon from silicone grease or silicone tubing.

Chosen PDMS fluids

PDMS fluids used in this study were three different linear PDMSs (silicone oils) provided by BlueStar® Silicones: a methyl-terminated PDMS (H 47V 1000) named 'M', a hydroxyl-terminated PDMS (H 48V 750) named 'H' and a vinyl-terminated one (621V 1500) named 'V'. The chosen PDMSs were not water soluble, not volatile, and they were different from each other in their chemical end groups (Table 1). The H PDMS is a (polydimethyl)siloxanediol. The generic formula of M, H and V PDMS is shown in Table 1, where n corresponds to the number of siloxane units and may vary from 10 to >10,000. The viscosity of PDMS generally increases as a function of increased chain length and is used to classify PDMS fluids (in the nomenclature, the number indicates the viscosity level in $\text{mm}^2 \text{s}^{-1}$ at 25 °C). The chosen PDMSs (M, H and V) have a medium viscosity. PDMS is not a single discrete compound, but a distribution of homologous structures with varying molecular weights. Little information is given in the technical data sheet. For instance, the average value of n is unknown. It was only found that the M PDMS has a molecular mass between 38,000 and 40,000 g mol^{-1} (BlueStar Silicones 2010).

Table 1 | Linear PDMS fluids studied: methyl-terminated (M), hydroxyl-terminated (H) and vinyl-terminated (V)

PDMS naming	End group chemical nature	Chemical structure	Physico-chemical characteristics				
			Viscosity at 25 °C ($\text{mm}^2 \text{s}^{-1}$)	Water solubility at 25 °C	Vapour pressure at 20 °C (kPa)	Volatile fraction at 150 °C (2 hours)	Density at 25 °C (kg m^{-3})
M	Methyl		1,000	Insoluble	<0.01	<0.2%	~970
H	Hydroxyl		750	Insoluble	<0.01	<1%	~973
V	Vinyl		1,500	Insoluble	<0.01	<1%	~980

Preliminary chemical degradation tests

Preliminary degradation tests were achieved with the three PDMS fluids (H, M and V). These batch degradation tests consisted in mixing each PDMS fluid with different aqueous solutions: 200 mL of aqueous solution were added to 10 g of polymer in sterile high density polyethylene (HDPE) 250 mL bottles. The mixtures were rotated at 10 ± 2 rpm at ambient temperature (24 ± 2 °C) for 15 days, without replication. Afterwards, the two phases (PDMS organic phase and aqueous phase) were separated using glass separatory funnels. Then, total Si concentration was determined in the aqueous phase, as described in the 'Total Si analysis' section below. The aqueous solutions in contact with PDMS were either alkaline (pH 9, 10 and 11), with sodium hydroxide (NaOH) or calcium hydroxide (Ca(OH)₂) addition, or acidic (pH 2, 3 and 4), with hydrogen chloride (HCl) or nitric acid (HNO₃) addition. For each PDMS, a 'blank sample' was prepared, by adding demineralised water.

Kinetic study

The kinetic study was performed using the methyl-terminated PDMS (M). Two hundred millilitres of aqueous solution were added to 10.00 ± 0.04 g of polymer in sterile HDPE 250 mL bottles. The aqueous solutions in contact with PDMS were demineralised water (measured pH = 5.7), NaOH solution (pH = 12.0), or HCl solution (pH = 2.0). The mixtures were rotated at 10 ± 2 rpm at ambient temperature (24 ± 2 °C) for fixed contact times (between 2 and 46 days). For each contact time and each aqueous solution, samples were prepared in triplicate. Afterwards, triplicate samples were sacrificed. The two phases were separated using glass separatory funnels. Then, total Si concentration was determined in the aqueous phase. Contact times were chosen to obtain Si concentrations in the aqueous phase every 2 or 3 days. Si concentration was also determined in the added solutions (without PDMS): demineralised water, NaOH solution and HCl solution (for baseline subtraction).

Choice of the analytical method to quantify PDMS degradation

In both the preliminary degradation tests and the kinetic study, PDMSs were suspended in aqueous solutions. Three phases coexisted in the closed HDPE bottles: an organic phase (PDMS), an aqueous phase and a gaseous phase. As mentioned

in the introduction, PDMS hydrolysis in the environment was of interest, especially in wastewater and landfill leachates. For this reason, it was chosen to quantify degradation products in the aqueous phase: as a result, only the water soluble degradation products are considered in this study.

Silicon chemistry is known to be complex and very different from carbon chemistry (Varaprath *et al.* 2006). Especially, organosilicon materials have a tendency to recombine at interfaces (Bischoff & Cray 1999). Moreover, degradation products are a distribution of compounds. Consequently, it would make no sense to analyse the speciation of all degradation products versus time. Besides, chromatographic methods can be used for identification (gas chromatography/mass spectrometry) but quantification is almost unfeasible because no standard exists for these compounds, except for some volatile siloxanes.

The main objectives were to know whether there was PDMS hydrolysis or not, to be able to quantify PDMS degradation in aqueous solutions, and to identify the pH conditions that favoured hydrolysis. Consequently, a global indicator for PDMS degradation was needed. The chosen method was the analysis of total Si in aqueous phase. This method allowed us to quantify the soluble part of the degradation products. Indeed, the chosen PDMS polymers being not water soluble meant Si found in the aqueous phases was the result of PDMS degradation or monomer release.

Total Si analysis

Total Si concentrations were determined in the aqueous phases by inductively coupled plasma–optical emission spectroscopy (ICP–OES) (Jobin – Yvon Horiba Ultima II) at the most sensitive emission line (251.611 nm). The uncertainty of measurement was less than 5%. An instrumental detection limit of 0.014 mg L^{-1} was achieved.

RESULTS AND DISCUSSION

Preliminary tests

The objective of these assays was to demonstrate PDMS degradation feasibility when in contact with aqueous solutions (in wastewater for instance). Batch degradation tests were performed on H, M and V polymers. In order to be as representative as possible of PDMSs likely present in wastewaters and landfill cells, H, M and V polymers were chosen for their intensive production. The results are summarised in Figure 1. In all added solutions (HNO₃, HCl,

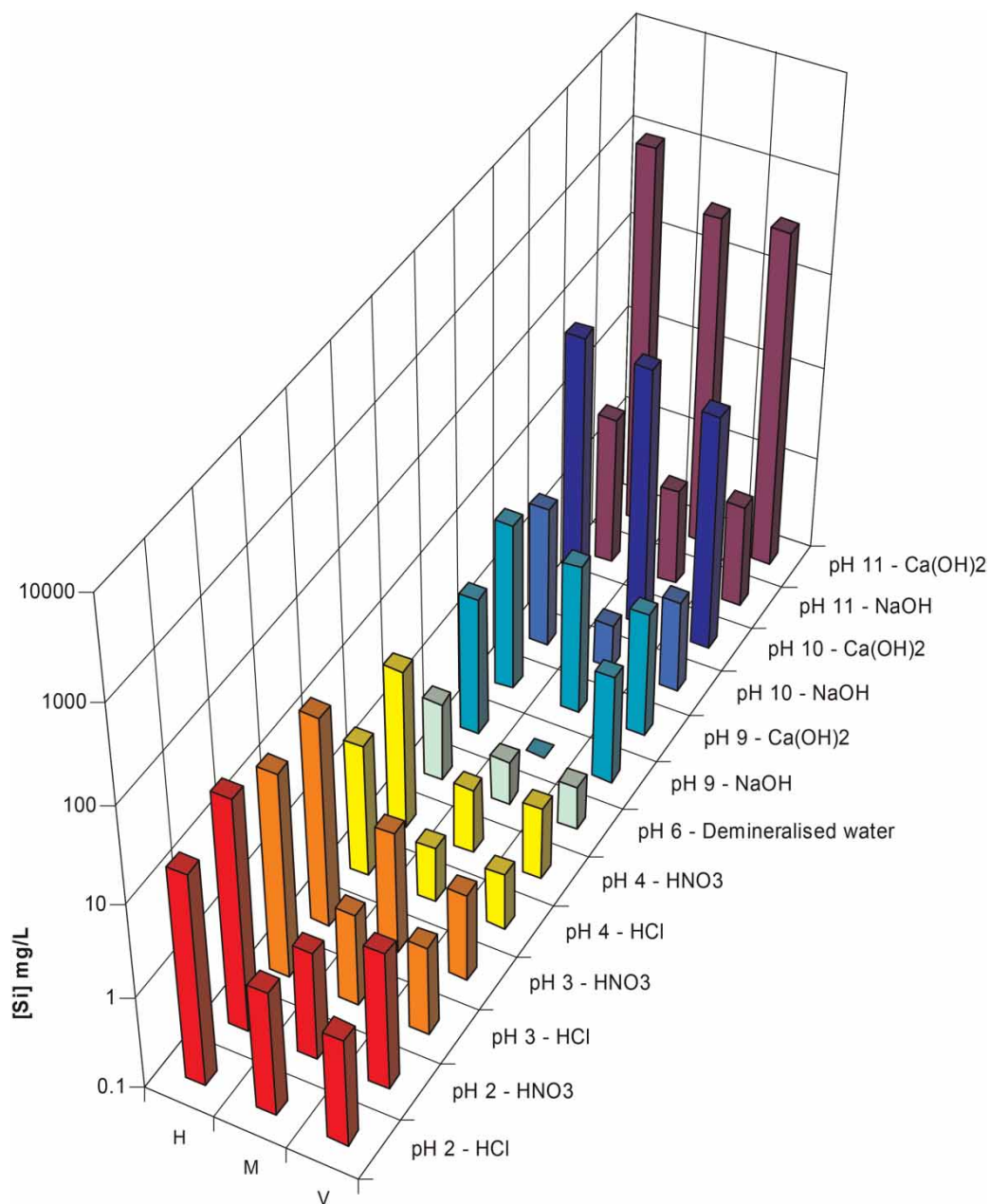


Figure 1 | Si concentrations (mg/L) in aqueous phases after 15 days' contact time with the demineralised water or acidic (HCl or HNO₃) or alkaline (NaOH or Ca(OH)₂) solutions for H, M and V PDMS fluids (the full colour version of this figure is available in the online version of this paper, at <http://www.iwaponline.com/wst/toc.htm>).

NaOH, Ca(OH)₂ solutions and demineralised water), the concentration of Si was below the detection limit.

It can first be observed that Si concentration in the demineralised water after 15 days' contact time with the PDMS was not null, whatever the PDMS polymer tested. This could be due either to a very low solubility of PDMS in water or to polymer degradation. It could also be due to the release of soluble non-polymerised monomers. Si

concentration in demineralised water (after 15 days' contact with PDMS) can be considered as a baseline. Other data (Figure 1) have shown that whatever the PDMS, the aqueous solution and the pH value, Si concentration was higher than in demineralised water (except for an outlier at pH 9, with the NaOH solution and the MPDMS). This demonstrated that PDMS fluids were degraded: during each assay, Si was released. The influence of pH was

significant. These results are consistent with those related by Spivack & Dorn (1994) who observed catalysis of PDMS hydrolysis by acid and base.

Concerning acidic conditions, the most acidic aqueous solutions induced the maximal degradation. Both of the used acids (HCl and HNO₃) induced similar degradation levels. The hydroxyl-terminated PDMS (H) was the most released in the aqueous phase. This is consistent with the end group nature of this polymer, which is more hydrophilic. In the case of HNO₃, degradation could also be partly due to an oxidative effect.

Concerning alkaline conditions, the hydroxyl-terminated PDMS was also the most degraded. In the same way, the most basic conditions induced the maximal degradation level. The degradation level was different for the two alkaline solutions: Ca(OH)₂ induced much more degradation than NaOH, whatever the pH value (Si concentration was about 300 times higher). Therefore, the degradation mechanism is not exclusively governed by pH: the alkaline nature and especially cation nature seems to be significant. Ca²⁺ was more effective than Na⁺ for promoting PDMS degradation. This observed catalytic effect of Ca²⁺ is consistent with studies relating to degradation of a PDMS fluid on clay minerals: degradation of PDMS on Na-saturated montmorillonite was very slow, but a change in the exchangeable cation from Na⁺ to Ca²⁺ increased the rate by 1.5-fold (Xu 1998). The highest degradation rate observed in these preliminary tests was obtained with the H polymer in contact with a Ca(OH)₂ solution at pH 11. Considering the mass of Si in the polymer initially introduced in the HDPE bottle was about 3.8 g, the fraction of released polymer in the aqueous phase corresponded to approximately 5.5–6.0% of Si. This value was probably underestimated due to a low proportion of hydrolysis products which were volatilised.

These results can be linked to those obtained in studies concerning the fate of PDMS in soils. Indeed, it was demonstrated at laboratory scale that PDMS in soils could hydrolyse to yield low molecular weight, water-soluble molecules: silanols and especially dimethylsilanediol (DMSD) (Lehmann *et al.* 1994, 2000). According to Graiver *et al.* (2003) in a review concerning PDMS degradation in the environment, high molecular weight PDMSs are initially depolymerised by hydrolysis of the siloxane bonds to yield organosilanol terminated oligomers (also called siloxanols, i.e. containing at least one SiOH end group). By analogy, it can therefore be supposed that hydrolysis products are similar in this study. Degradation products present in

aqueous matrices are supposed to be polar compounds, such as siloxanols.

Kinetic study

A degradation kinetic study was performed during 46 days using the methyl-terminated PDMS (M) as methyl-terminated are the most industrially used PDMSs. HCl (pH 2) and NaOH (pH 12) were chosen as acidic and alkaline media, respectively. HCl was chosen instead of HNO₃ to avoid the possible oxidative effect of HNO₃. In the same way, as an enhancement in degradation was observed in the presence of Ca²⁺, in order to study the pH effect and avoid side effects, NaOH was chosen instead of Ca(OH)₂. Average Si concentrations from triplicates in the aqueous phase are plotted as a function of contact time in Figure 2. Average standard deviation of triplicates was 0.02 mg L⁻¹ in demineralised water, 0.14 mg L⁻¹ in acidic conditions and 0.85 mg L⁻¹ in basic conditions. The error bars on Figure 2 include both standard deviation and uncertainty on Si concentration due to ICP-OES analysis.

The highest degradation rate was obtained with the NaOH solution (Si concentration is around 14 mg L⁻¹ after 42 days, corresponding to 0.07–0.08% of the Si initially present in the bottle). Then, in the HCl solution, after 46 days, around 3.5 mg Si L⁻¹ were released in the aqueous phase due to PDMS degradation. In demineralised water, Si concentration was above detection limit but remained very low.

From these results, degradation reaction order was investigated. Figure 2 suggests zeroth-order kinetics. This is consistent with the fact that only the very beginning of the degradation kinetics was studied. Consequently, whatever the reaction order, at the very beginning, degradation probably follows a pseudo-zeroth-order kinetic. Reaction rate constants at 24 °C were estimated to 0.28 mg Si L⁻¹ day⁻¹ in alkaline solution, 0.07 mg Si L⁻¹ day⁻¹ in acidic solution and 0.002 mg Si L⁻¹ day⁻¹ in demineralised water.

For alkaline degradation, from day 14, some triplicate samples were cloudy. Consequently, they were not taken into account. A micro-emulsion had probably formed. Indeed, after several days of settling, in some cases, the aqueous phase became clear. This phenomenon could be explained by the possible presence of micelles, composed of hydrophobic siloxanoate backbones and hydrophilic end-groups Na⁺-O-Si. As a consequence, in that case, it was not possible to determine if the Si concentration in the aqueous phase was due to the presence of soluble degradation products or to the formation of invisible micelles.

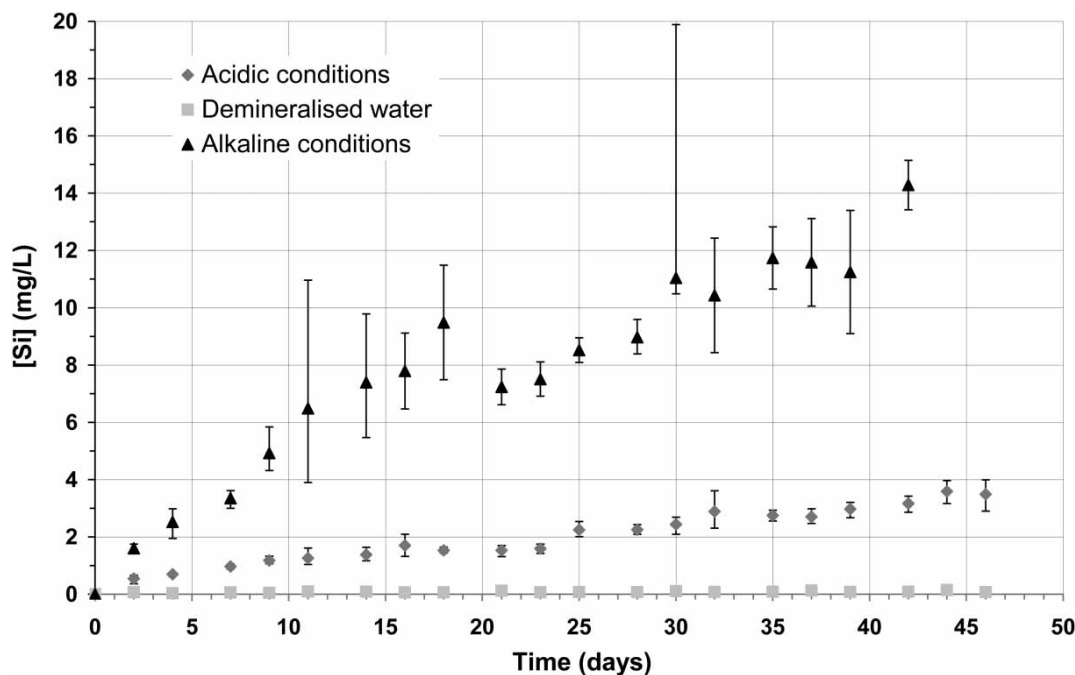


Figure 2 | Evolution of Si concentrations in aqueous phases for the three tested conditions: acidic (pH = 2), demineralised water (pH = 5.7), alkaline (pH = 12) – Temperature: 24 ± 2 °C – Error bars include standard deviation and uncertainty in Si concentration.

In the case of alkaline degradation, the general trend is an increase in Si concentration in the aqueous phase; however, Si concentration seems to oscillate. This tends to show that chemical equilibria are reached between PDMS depolymerisation and repolymerisation by condensation of lower weight entities, as already observed by Spivack & Dorn (1994). It is also possible that the same phenomenon occurs for acidic degradation.

The previous remarks can be linked to results from preliminary tests, where the counter-ion of the alkaline compound plays a predominant role. Indeed, there is equilibrium between hydrolysis and condensation. Due to the counter-ion, degradation products may be stabilised and equilibrium may be displaced. So this ion may influence PDMS degradation by decreasing the rate of siloxane chain repolymerisation by condensation, or by promoting emulsion formation in the aqueous phase (as suspected in the NaOH solution).

Discussion: PDMS degradation in WWTP and landfill cells

Although the obtained results cannot be directly extrapolated (especially because extreme pHs were used to accelerate the degradation), in both WWTP and landfill cells, favourable conditions for degradation can be obtained

temporally or locally (pH, presence of Ca^{2+} cations). At less extreme pHs, the hydrolysis is slower, but there is a wide variety of compounds that possibly have a catalytic effect on the degradation.

In WWTPs, the residence time in digesters is typically in the order of 30 days. High PDMS levels and extreme pHs can be obtained locally in the sewer network but not in the digester. High Ca^{2+} concentrations can be obtained, depending on water hardness. High molecular weight PDMSs are probably little hydrolysed, but a large part of PDMSs present in wastewater, coming from detergents, shampoo and cosmetics for instance, have a lower molecular weight than the ones studied in this paper and are more quickly hydrolysed to form small and volatile compounds. Indeed, a large proportion of volatile siloxanes is sorbed on to activated sludge (Fendinger *et al.* 1997).

In landfill cells, residence time is very high (several 10 years), leachates can be acidic or basic (range 4.5–9.0) depending on the degradation stage of the landfill (Öman & Junestedt 2008), with a strong presence of cations such as Na^+ and Ca^{2+} , with concentrations range from 70 to 7,700 and 10 to 7,200 mg L^{-1} , respectively (Christensen *et al.* 2001). This could enable the hydrolysis of high molecular weight PDMSs. Moreover, high polymer levels are locally possible. These conditions promote PDMS hydrolysis into hydrophilic (water soluble) compounds such as

siloxanols. Biodegradation may also occur (Graiver *et al.* 2003; Ohannessian *et al.* 2008) and the final degradation products could be silanols (including trimethylsilanol (TMSol) and DMSD). These assumptions are corroborated by Grümping & Hirner (1999) who analysed leachates from different waste deposit sites. They could detect DMSD in almost all samples in the low milligram per litre range, and it was furthermore possible to determine TMSol in some leachate samples in the microgram per litre range. Badoil & Benanou (2009) identified 1,1,3,3,5,5-Hexamethylsiloxane-1,5-diol and 1,7-dihydroxy-1,1,3,3,5,5,7,7-octamethylsiloxane in landfill leachates. TMSol is volatile but the other three are not. Non-volatile silanols condensation can generate linear and cyclic siloxanes such as hexamethyldisiloxane (L2), hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4) or decamethylcyclopentasiloxane (D5), which are volatile and can subsequently be found in biogas. Indeed, the silanol group has a strong tendency to undergo self-condensation reactions to give compounds containing the siloxane linkage (Si–O–Si) (Purkayastha & Baruah 2004; Varapath *et al.* 2006). That is the reason why Paxéus (2000) could detect L2, D3, D4 and D5 in municipal landfill leachates.

These elements confirm that VOSiCs in sewage and landfill biogas arise from silicones or/and their degradation products in wastewater and solid waste.

CONCLUSIONS

The experiments presented in this paper have shown the influence of pH conditions on PDMS hydrolysis. The most extreme pH values induce the highest Si concentrations in the aqueous matrices. Moreover, alkaline conditions seem more favourable for hydrolysis. But two other parameters also play a role: the nature of the PDMS end-group (with a higher degradation for hydroxyl-terminated PDMS) and, in alkaline conditions, the nature of the counter-ion. A complete kinetic study of PDMS degradation is difficult to achieve (due for instance to the apparition of microemulsions) and lab-scale experiments (in extreme pH conditions) showed that after 46 days, degradation still occurred.

Chemical degradation is possible in landfill cells and WWTPs where chemical conditions promote PDMS hydrolysis into hydrophilic compounds such as siloxanols. A combination of complete hydrolysis, biodegradation and self-condensation of silanols could lead to the formation of

low molecular weight and volatile molecules that can subsequently be found in biogas.

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