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Perchlorate Leaching from Solid Rocket Motor Propellant in Water

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Several launch vehicle solid rocket motor propellants contain ammonium perchlorate as a major ingredient, and so the potential exists for perchlorate release to the environment during launch operations and propellant manufacture. Solid composite base propellants containing four types of binder were studied: hydroxyl-terminated polybutadiene, carboxyl-terminated polybutadiene, polybutadiene-acrylic acid-acrylonitrile terpolymer, and polyurethane. The rate of perchlorate release from solid propellant during immersion in deionized and simulated seawater has been measured at 5, 20, and 29°C. The rate-limiting step is most probably diffusion, and the diffusion coefficient is given. Arrhenius terms are presented to facilitate calculation of diffusion coefficients at intermediate temperatures. The diffusion coefficients for all propellant types and conditions tested fall in the range from 3.6×10^{-12} to 1.1×10^{-13} m^2 s^{-1}. The diffusion coefficients for each propellant type are proportional to temperature and inversely related to salinity.

Nomenclature

A = preexponential factor
D = diffusion coefficient
E_a = activation energy
$f_{ClO_4^-}$ = fraction of perchlorate lost from propellant
R = molar gas constant
r = radius
T = temperature, Kelvin
t = time
$(\Delta x)_{rms}$ = root mean squared distance traveled by diffusing molecule
τ = characteristic diffusion time

Introduction

PERCHLORATE is an important ingredient in solid rocket motors; it acts as the oxidizer and often composes more than 50% of the propellant by weight.[1] Although precautions and safeguards are in use, the prevalence of perchlorate in solid rocket motors creates a potential for its release to the environment. This could happen in propellant manufacture, transport to the launch site, or during launch operations. Of particular concern is perchlorate release in wetlands and fish breeding habitats. The U.S. Environmental Protection Agency has recently identified the perchlorate ion (ClO_4^-) as a contaminant in the environment.[2] To enable better understanding of environmental issues related to perchlorate-containing solid propellants, a study was undertaken to determine the rate at which perchlorate is released from solid propellant immersed in water and the influence of temperature and salinity on the rate. These measurements are most relevant to a launch anomaly or other process that drops unburned propellant into a large body of fresh water or the ocean.

The perchlorate release rate from immersed solid propellant is measured. Diffusion of water into the propellant matrix is thought to be the rate-limiting process in the mechanism of perchlorate release from submerged propellant. We present a diffusion coefficient that can be used in modeling perchlorate releases from propellant. This study includes propellants characterized by four different types of polymeric binders: hydroxyl-terminated polybutadiene (HTPB), carboxyl-terminated polybutadiene (CTPB), polybutadiene-acrylic acid-acrylonitrile terpolymer (PBAN), and polyurethane (PU).

Previous Studies

The effects of water and humidity on various solid propellants containing ammonium perchlorate have been previously studied.[3–6] In most studies, the focus was on either the effect of water on the propellant material properties or on methods for recycling perchlorate. Some data exist on the diffusion constant for propellant in deionized water and on propellant weight loss in salt water. However, the database is lacking sufficient data for comparing the rate of perchlorate release from solid propellant immersed in fresh water and salt water at a range of temperature conditions. A brief summary of two of the studies follows.

A study by Merrill and Drobinak[3] looked at several aspects of submerged samples of graphite epoxy motor (GEM) II HTPB propellant. Samples were placed in circulating Pacific seawater, simulated seawater, and in deionized water. Samples were 1 (2.54)-, 2 (5.08)-, 4 (10.16)-, and 15 (38.1)-in. (cm) cubes. Some samples were buried in sand; the ammonium perchlorate release rate was very similar for buried and unburied samples. Samples were dried after immersion to determine ammonium perchlorate loss by weight. Data are presented graphically. During the course of the study, it was observed that unburied propellant surfaces became slippery and slimy, suggesting biological activity. It was observed that specimens swelled in volume with exposure time. Crystals of ammonium perchlorate were observed on the outside of dried samples. Hazard tests conducted on immersed, then dried samples showed that the outer surfaces were less likely to ignite under friction and impact than virgin propellant, and the inner part was slightly less likely to ignite than virgin. Exposed samples would still burn when put into fire.

A study by McIntosh et al.[4] demonstrates that solid propellant in water can be made to release perchlorate. Recovery of ammonium perchlorate from the propellant was shown to be 96–98%. This study looked at aqueous extraction of perchlorate from solid propellant. They demonstrated the feasible recovery of ammonium perchlorate from propellant. Thin pieces of propellants TP-H1011 (PBAN family) and ANB-3066 (CTPB), 1 × 1 in. (2.54 × 2.54 cm), with a thickness from 0.2 to 0.006 in. (0.51 to 0.015 cm), were extracted with a high-speed propeller stirrer into a solution containing a dispersing agent and an initial concentration of 14% ammonium perchlorate in water at 82°C (180°F) for 15 min.

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Table 1 Weight percent of perchlorate in propellant specimens used in this study

Binder type	Ammonium perchlorate NH_4ClO_4, %	Perchlorate ClO_4, %
CTPB	73.0	61.8
HTPB	69.0	58.4
PBAN	69.8	59.1
PU	65.4	55.3

Experimental Methods

To determine the rates at which perchlorate is released from solid propellants in water, specimens of different propellant types were immersed in water of known temperature and salinity, and the perchlorate concentration of the water monitored over time.

Four types of perchlorate propellant, identified here by their binder type, were used in this study: HTPB, CTPB, PBAN, and PU. The U.S. Air Force Research Laboratory, Space and Missile Propulsion Branch, Edwards Air Force Base, California provided the propellant samples. Table 1 summarizes the concentrations, by weight percent, of the perchlorate in the specimens used in this study.

Specimens of each solid propellant type were prepared by blade cutting and using a blade cork-borer tool. Specimens were cylindrical in shape, with a height of approximately 14 mm and diameter of approximately 14 mm (~2.2 ml in volume). The weight of each specimen was approximately 4 g. The PU is the hardest of the four types of propellant in this study. It was found to be difficult to blade cut. Fewer specimens of PU were used than the other propellant types because of these handling problems.

The specimens were held immersed in 500 ml of water in individual containers at controlled temperature. The temperatures chosen for this study (5, 20, or 29°C) approximate the range of seawater temperatures found from Alaska to Florida. The standard deviation of the temperatures during the study was less than 1°C. The water salinity was either deionized water, ~10 MΩ (pure) or a simulated seawater (salt) prepared from a commercial product for aquarium use, Instant Ocean®.[7] Actual seawater was not used because it contains biological elements with maintenance requirements beyond the scope of this study. This study did not attempt to measure or control biological conditions. Samples were not actively mixed while being held between analyses, but experienced some mixing effects as a result of vibrations from the temperature control chambers. The HTPB specimen in the 29°C simulated seawater was omitted due to a handling error.

Periodically over the course of 12 weeks, the containers were opened and an aliquot of the liquid analyzed to determine the concentration of perchlorate that had diffused from the propellant. Aliquots varied from 5 ml at the beginning of the study to 1 ml at the end; accurate readings of low concentrations required a larger sample size.

The concentration of perchlorate in the water was measured using a perchlorate ion-specific electrode. Samples were mixed immediately before the withdrawal of an aliquot for analysis. Aliquots were typically diluted before analysis.

The manufacturer's[8] recommended method for the determination of perchlorate was followed. Fresh standards were prepared for each analysis. Ionic strength adjuster was added to standards and samples after dilution to known volume. A comparison of standard curves run with deionized water and with simulated seawater showed that the salts present in the simulated seawater samples did not interfere with the response of the perchlorate electrode. All samples analyzed contained perchlorate at parts per million levels. The concentration of perchlorate ion in solution in the sample container was calculated from the aliquot concentration and dilution factors. From the measurement of the concentration of the perchlorate ion in solution, the mass fraction loss of the propellant sample due to perchlorate release was calculated.

The laboratory measurements of perchlorate concentrations in the water were used to calculate the amount of perchlorate released by the propellant specimen as a fraction of the original mass of perchlorate in the specimen. Measurements for each specimen were repeated over 12 weeks to provide sufficient data to establish a perchlorate release rate for each specimen at the given temperature and salinity conditions.

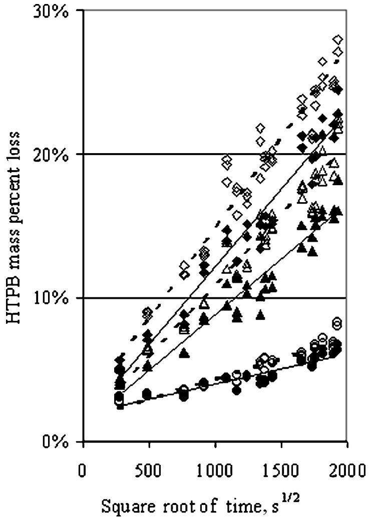

Fig. 1 **Typical results, fraction of perchlorate extracted vs square root of time for HTPB. ○, 5°C; △, 20°C; and ◇, 29°C; data from deionized water are shown as open symbols (dotted lines), simulated seawater data are shown as filled symbols (solid lines), lines are linear fits to data.**

Results

All types of propellant tested released perchlorate while immersed in simulated seawater and in deionized water. The fastest rate of perchlorate release was from propellant type PU, followed by HTPB, PBAN, and CTPB.

The rates were significantly influenced by the temperature and salinity of the surrounding water. The results for all propellant types show a correlation of increased rate of perchlorate release with increased temperature.

The results show that at each temperature, each propellant type released perchlorate at a faster rate in deionized (pure) water than in the simulated seawater (salt). The effect of salinity is to reduce the rate of perchlorate loss from the sample. Rates in simulated seawater are roughly 15–25% slower than rates in deionized water.

Figure 1 shows typical results for HTPB propellant. In Fig. 1 the x axis shows the square root of the time. The y axis is the mass fraction of perchlorate that has left the specimen. A y-axis value of unity would indicate that all excess perchlorate has left the specimen. (Although the specimen would still contain perchlorate at a concentration equal to that in the surrounding water.) Figure 1 shows that the specimen in deionized water at 29°C released perchlorate at approximately five times the rate of the specimen in simulated seawater at 5°C.

The linear fit of mass fraction of perchlorate to the square root of time indicates that the loss mechanism is consistent with diffusion-limited phenomena.[9] The nature of the processes responsible for the leaching of propellant, and their contributions to the rate, will be presented in detail in the discussion section.

The results from PU in deionized water at 29°C provide a measure of the experimental error in the method. For this sample, the measurements of perchlorate fraction loss level off after 2000 $s^{1/2}$ (approximately 7 weeks). This indicates there is no longer a net extraction of perchlorate from the sample. Nearly all of the excess perchlorate has been extracted from the specimen; the concentration of perchlorate remaining in the propellant is equal to the perchlorate concentration in the surrounding water. This level off in the perchlorate fraction loss measurements should be observed slightly below unity. For this sample, it occurs at 5–10% above unity. This 5–10% difference can be regarded as the experimental error, indicating good accuracy for the method.

Diffusion Coefficients

Data from all of these specimens can be used to calculate a diffusion coefficient for propellant type, temperature, and salinity

Table 2 Diffusion coefficients (square meters per second) for perchlorate release from HTPB, CTPB, PBAN, and PU solid propellants immersed in deionized water and simulated seawater at 29, 20, and 5°C

T, °C	Deionized water	Simulated seawater
	CTPB	
29	$1.31E{-}12$	
29	$1.27E{-}12$	
20	$9.86E{-}13$	$4.31E{-}13$
5	$4.04E{-}13$	$1.39E{-}13$
5	$3.58E{-}13$	
	HTPB	
29	$1.51E{-}12$	
29	$1.53E{-}12$	
20	$1.07E{-}12$	$7.71E{-}13$
5	$3.87E{-}13$	$2.78E{-}13$
5	$3.74E{-}13$	
	PBAN	
29	$1.83E{-}12$	$1.21E{-}12$
29	$1.42E{-}12$	
20	$1.33E{-}12$	$8.28E{-}13$
5	$5.99E{-}13$	$4.24E{-}13$
5	$6.91E{-}13$	
	PU	
29	$3.57E{-}12$	$1.80E{-}12$
5	$1.31E{-}12$	$5.39E{-}12$

condition. The diffusion coefficient can be used to compare propellants and in modeling perchlorate release. The legitimacy of using a diffusion coefficient to characterize this process will be discussed later.

Diffusion is the process whereby material is transported as a result of random molecular motion. Although individual molecules move randomly, there is an average movement from areas of high concentration to areas of low concentration. The Einstein–Smoluchowski equation gives the rms distance traveled by a diffusing molecule and shows the square-root relationship characteristic of the process,

$$(\Delta x)_{\mathrm{rms}} = \sqrt{2Dt} \tag{1}$$

Diffusion coefficients$^{9-12}$ for the release of perchlorate from solid propellant immersed in water were calculated from the laboratory data analytically using Bessel function series, assuming Fickian diffusion for HTPB, CTPB, PBAN, and PU. Table 2 lists the diffusion coefficients for the four types of propellants studied.

The diffusion coefficient can be employed to model propellant perchlorate release. The characteristic diffusion time corresponds to the time required for a concentration decrease to $1/e$ of its original value.[13] For a sphere, this time can be calculated from the following expression[14]:

$$\tau = r^2/\pi^2 D \tag{2}$$

For materials that have a constant diffusion coefficient, this expression can be used to calculate the characteristic diffusion time for spheres of various radii.

When the concentration decreases to $1/e$ of its original value, this equates to a release of 63.2% of the perchlorate from the sample. Using this in the following equation provides a convenient means to calculate the fractional loss of perchlorate for various sample sizes at various times:

$$f_{\mathrm{ClO}_4} = \sqrt{(t/\tau)} \times 0.632$$

Temperature Dependence

The Arrhenius expression (see Ref. 15) can be used to extrapolate diffusion coefficients at other temperatures. If we substitute the diffusion coefficient for the rate constant in the Arrhenius expression, we obtain

$$D = A\exp(-E_a/RT) \tag{3}$$

Table 3 Activation energies E_a (kilo calories per mol)

Binder	Deionized water	Simulated seawater
HTPB	9.7 ± 2.1	11.0 ± 3.0
CTPB	8.4 ± 1.5	12.3 ± 2.5
PBAN	6.3 ± 3.0	8.7 ± 1.1
PU	6.3 ± 2.3	7.7 ± 2.1

Table 4 Terms for Arrhenius[a] fit of diffusion coefficients

Binder	Water	E_a/R	A
HTPB	Deionized	$-4.900E{+}03$	-10.934
HTPB	Simulated seawater	$-5.545E{+}03$	-8.975
CTPB	Deionized	$-4.208E{+}03$	-13.366
CTPB	Simulated seawater	$-6.203E{+}03$	-7.264
PBAN	Deionized	$-3.169E{+}03$	-16.604
PBAN	Simulated seawater	$-4.371E{+}03$	-12.883
PU	Deionized	$-3.171E{+}03$	-15.860
PU	Simulated seawater	$-3.851E{+}03$	-14.287

[a] $\ln D = (E_a/R)(1/T) + A$.

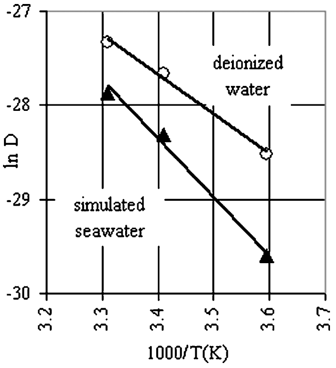

Fig. 2 Arrhenius plot of CTPB diffusion coefficients in ○, deionized water and ▲, simulated seawater.

Activation energies calculated for each propellant are shown in Table 3, along with uncertainties of two standard deviations. For the HTPB and PU simulated seawater runs, there were too few points to calculate an uncertainty, and so the uncertainty was estimated as the average percent uncertainty for the other samples.

The Arrhenius expression gives a linear relationship between the logarithm of rates and the inverse of their absolute temperature. Figure 2 shows an Arrhenius plot for the diffusion coefficients of HTPB in deionized water and in simulated seawater.

Table 4 lists the terms of a least-squares fit to an Arrhenius plot for each type of propellant tested in simulated seawater and in deionized water. One can use the terms from the linear fit to calculate diffusion coefficients at various temperatures.

Calculations of characteristic diffusion time based on diffusion coefficients obtained for HTPB in simulated seawater can be compared to the values obtained by extrapolating data from a study conducted by Merrill and Drobinak[3] of an HTPB propellant in seawater. That experiment studied 1-, 2-, and 4-in. cubes of an HTPB propellant in a 10,500 gall pool of seawater at an average temperature of 71.5°F. Insufficient data were reported to do a comparison on the 15-in. cubes. The experiment stopped before the $1/e$ time was reached, but that time may be estimated by extrapolating the existing data against the square root of time. Good agreement is shown when these data are compared to calculated characteristic diffusion time of 1-, 2-, and 4-in.-diam spheres using the diffusion coefficients for HTPB specimens adjusted for temperature.

Some previous studies inferred the perchlorate loss by performing weight loss measurements. In those studies, the total mass fraction loss of a sample would include, in addition to the mass fraction loss of perchlorate, the loss of the ammonium ion, the loss of the other water-soluble constituents, and may include the physical loss of some insoluble constituents. In this work, we observed shedding of the outer layers of binder from some samples at long times.

Incomplete drying could also influence the weight loss method. The method in this work would not be influenced by these factors, but could be affected by other factors such as the performance of the electrode, accuracy of the standard, or interference of other ions. For each method, these factors can be accounted for in the analysis, or controlled by adherence to careful procedures. The good agreement between diffusion coefficients measured in this work and data from the previous studies increases the confidence in both methods.

Discussion

In the current experiment, the loss of perchlorate was observed. Leaching of perchlorate from propellant binders by water is a complicated phenomenon. It requires the penetration of water into the matrix, the dissolving of the perchlorate salt, and the transport of the perchlorate out of the matrix. There may be additional complicating processes such as the relaxing of the polymer matrix as it is solvated by water. The measured rate could be governed by any one of these mechanisms, or a combination.

The diffusion of water in polymers itself is not a simple process. In addition to penetrating and moving through the matrix, the water can solvate and relax the polymer chain, modifying the polymer matrix. In the current measurement samples became swollen with time; this is an indication of polymer solvation, but the degree of swelling was not quantified in this experiment. These modifications to the polymer matrix may enhance or inhibit the transport of water compared to the original matrix, altering the diffusion coefficient. The resulting diffusion behavior may be Fickian, non-Fickian, or case 2, depending on the relative rates of the diffusion, relaxation, and solvation processes.[16–18] The absorption process also perturbs the water by altering the hydrogen bonding network.[19] The current experiment is further complicated by the presence of the perchlorate salt, which dissolves in the water and leaves the matrix. As shown in Table 1, the perchlorate is more than 50% by weight of the propellant; the loss of such a major component will surely perturb the matrix.

In the model developed here, the diffusion of water into the polymer matrix is the slow or rate-limiting step and is consistent with the rate of diffusion of water measured in other polymers. Once wet, the perchlorate salt rapidly dissolves, and the perchlorate ions are rapidly transported out of the propellant. The wetted polymer rapidly relaxes, swelling the matrix and admitting more water, which helps to speed the dissolution and transport of the perchlorate salt. The voids left in the matrix by the departing perchlorate also help ensure that the departure of subsequent perchlorate ions will be unimpeded.

Despite the complicated nature of the leaching process, the data show a linear dependence on the square root of time, indicating that the kinetics is relatively simple. This only occurs when one of the processes is much slower than all of the other processes.[16–18] The evidence in this experiment indicates that the diffusion of water into the matrix is the rate-limiting step in the leaching process under study here. This evidence will be discussed here.

First, the leaching process measured here is Fickian with a 0.5 exponent over the course of 12 weeks; this indicates that diffusion is the slow or rate-controlling step.[16,18] In cases where more than one process governs the rate of an observed change, the time dependence of the product rate deviates from the Fickian behavior seen here. This deviation can either speed up or slow down the observed rate depending on the interaction of the component rates,[16] but the probability of maintaining the linear Fickian time dependence is very small.

Second, the diffusion coefficients measured here are similar to values determined for water diffusing into other polymers by many different means. Our measurements fall between $1.1E{-}13$ and $3.6E{-}12$ $\mathrm{m^2/s}$, which is in the range of other measurements for water diffusing into polymers. Examples are from $1E{-}13$ to $3E{-}11$ $\mathrm{m^2\ s^{-1}}$ for water diffusing into segmented polyetherurethanes, from $1.3E{-}12$ to $2.4E{-}12$ $\mathrm{m^2\ s^{-1}}$ for poly-3-hydroxybutyrate,[17] and from $2.1E{-}11$ to $3.1E{-}11$ $\mathrm{m^2\ s^{-1}}$ for poly (vinyl-alcohol).[20] This overlap in measured rates is another indication that the diffusion of water into the polymer is the process being measured here.

Table 5 Comparison of calculations of characteristic diffusion time (seconds) using diffusion coefficients obtained for HTPB in simulated seawater to values obtained by extrapolating data by Merrill and Drobinak of HTPB propellant in seawater

Calculated from diffusion coefficients		From other HTPB study	
Sphere diameter, in.	This work	Cube edge, in.	Merrill and Drobinak study
1	$1.9E{+}07$	1	$2.2E{+}07$
2	$7.5E{+}07$	2	$5.7E{+}07$
4	$3.0E{+}08$	4	$2.6E{+}08$

Third, there is evidence that the other processes contributing to the leaching are much faster than the diffusion of water into the polymer. The diffusion constant of perchlorate in water is $1.792E{-}9$ $\mathrm{m^2/s}$ (Ref. 21). This is roughly 1000 times faster than the rates we measured here. In addition, the solubility of perchlorate in water at these temperatures ranges from 10 to 20% by weight; this suggests that dissolving the perchlorate in the water is not a bottleneck in the leaching rate observed here.

Fourth, the leaching rate scales with sample size in a manner consistent with diffusion. Although it is true that our samples were of a single size (14-mm diameter), we compared our measured diffusion constants to the data of Merrill and Drobinak who used samples of 1 in. (25.4 mm), 2 in. (50.8 mm), and 4 in. (101.6 mm) diameters.[3] As seen in Table 5, the rates extrapolated from our diffusion constants are within 15–30% of the rates measured by Merrill and Drobinak. The largest samples have a diameter seven times that used in this work. That our extrapolated diffusion coefficients hold over this size range is further evidence that diffusion of water into the polymer matrix is the rate-limiting step in the leaching of perchlorate by water from propellant samples.

The leaching rates of propellant in simulated seawater are consistently from 15 to 25% slower than in deionized water. There are several factors that could contribute to this. The concentration of water is lower in the simulated seawater, and this would give a smaller driving force to the diffusion. The salt concentration is only about 3%, however, which is not enough to explain the magnitude of the effect. The activity of the water in the simulated seawater is reduced to a greater extent, and this could explain the effect. The viscosity of seawater is also higher, which can decrease diffusion constants according to the Stokes–Einstein equation. Viscosity effects are usually associated with a solvent impeding the motion of a solute. Because we believe this measurement is of the water moving through the polymer matrix, it is unclear what effect the viscosity will have. A combination of the effects mentioned here may explain the slower diffusion rate in simulated seawater, but it is unclear from the current data. Diffusion measurements over a range of salt concentrations may help elucidate the reason for the slower diffusion of simulated seawater.

It is not clear what physical process is reflected in the activation energy. Because the diffusion of water into the polymer is the rate-limiting step, the activation energy is probably associated with that step. A likely explanation is that the activation energy represents the initial repulsion between the water and the binder lattice. The activation energy is lowest for PU, which is the most hydrophilic of the polymers tested. Tests with a wider range of polymeric materials would shed more light on the source of the activation energy.

Conclusions

The rates of extraction of perchlorate from four types of solid propellant immersed in waters of different salinity and temperature conditions have been measured. It was found that the extraction rate is consistent with diffusion of water into the polymer matrix as the rate-limiting step. The diffusion constant increases with increasing temperature and decreases with increasing salinity. The fastest extraction rate was observed at the highest temperature and lowest salinity. The perchlorate diffusion coefficients have been measured for samples of HTPB, CTPB, PBAN, and PU solid rocket motor propellant in deionized water and simulated seawater. The diffusion coefficients for all propellant types and conditions tested fall in the range from 3.6×10^{-12} to 1.1×10^{-13} m^2 s^{-1}. Arrhenius terms were presented to facilitate calculation of the diffusion coefficient at intermediate temperatures. Characteristic diffusion times calculated for 1-, 2-, and 4-in.-diam spheres of HTPB were calculated and showed good agreement with the results of another study. The mechanism of the perchlorate release was not investigated, but the results are consistent with the diffusion of water into the polymer matrix being the rate-controlling step.

Acknowledgments

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