

# IRON-INDUCED EFFICIENT DECOMPOSITION OF PERCHLORATE USING PRESSURIZED HOT WATER

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## Introduction

Perchlorate has been reported to occur in aquatic environments, drinking water and foodstuffs, and in humans<sup>1-8</sup>. The ammonium and potassium salts of  $\text{ClO}_4^-$  are used as oxidizers in jet and rocket fuels, pyrotechnic devices, explosives, fireworks, vehicle air bag inflators and so forth. Improper treatment of wastes associated with manufacture and use of these products can act as significant stationary sources of  $\text{ClO}_4^-$  in the environment<sup>6</sup>. Furthermore, sources attributable to industrial effluents<sup>7</sup>, fireworks manufacturing operations<sup>5</sup>, and fireworks displays<sup>3</sup> were recently indicated. Therefore, development of decomposition technologies for  $\text{ClO}_4^-$  to harmless  $\text{Cl}^-$  under mild condition is desired as a measure against stationary sources of emission.

Recently, reactions with pressurized hot water (PHW) have been recognized as an innovative and environmentally benign technique in water treatment. PHW is defined as hot water at sufficient pressure to maintain the liquid state, below the critical point of water (374 °C, 22.1 MPa). PHW has many characteristics that are favorable for chemical reactions: high diffusivity, low viscosity, and the ability to accelerate acid- and base-catalyzed reactions<sup>9</sup>.

In this study, we examined decomposition of  $\text{ClO}_4^-$  in PHW up to 300 °C, and examined the effect of several zerovalent metals in the reaction system<sup>10</sup>. Among metals we tested, iron led to the most efficient decomposition of  $\text{ClO}_4^-$  to  $\text{Cl}^-$  ion, with no formation of other chlorinated species such as chlorate ( $\text{ClO}_3^-$ ) and chlorite ( $\text{ClO}_2^-$ ). We also applied this method to the decomposition of a  $\text{ClO}_4^-$  contaminated water sample from a man-made reflecting pond, following fireworks display in Albany, New York<sup>3</sup>.

## Materials and methods

A stainless steel high-pressure tube reactor (11 mL volume) equipped with two stainless steel screw caps was used. In a typical run, an argon-saturated aqueous (Milli-Q water) solution (3.5 mL) of  $\text{ClO}_4^-$  (101–204  $\mu\text{M}$ ) and metal powder (0.91 mmol) were introduced into the reactor under an argon atmosphere by use of a globe bag, and the reactor was sealed. Then the reactor was placed into an oven, and the reactor temperature was raised at a rate of ca 10 °C  $\text{min}^{-1}$  to the desired reaction temperature (80–300 °C), and the temperature was held constant for a specified time (e.g., 6 h). After the specified time, the reactor was quickly cooled to room temperature. The reactor was opened, and the reaction mixture was centrifuged to separate the reaction solution and the solid phase (metal powder). The reaction solution was analyzed by ion chromatography for the quantification of residual  $\text{ClO}_4^-$  and the product,  $\text{Cl}^-$ , and other ionic species, if present.

The decomposition of  $\text{ClO}_4^-$  in water from a man-made reflecting pond following fireworks display was also examined. To decompose  $\text{ClO}_4^-$  in this sample, iron powder (1.82 mmol) was added to the sample (3.5 mL) and

the mixture was introduced into the reactor, and then reacted in the same manner as described above. Quantification of  $\text{ClO}_4^-$  in the samples before and after the reactions was carried out by liquid chromatography-tandem mass spectrometry (LC-MS/MS) at Wadsworth Center, New York State Department of Health, where the samples were analyzed immediately before and after the reaction experiments. Other major ions present in the sample prior to the reaction ( $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ) were measured by ion chromatography.

The ion-chromatograph system (Tosoh IC-2001) consisted of an automatic sample injector (injection volume: 30  $\mu\text{L}$ ), a degasser, a pump, a guard column, a separation column (Tosoh TSKgel Super IC-AP), a column oven, and a conductivity detector with a suppressor device. The mobile phase was an aqueous solution containing  $\text{NaHCO}_3$  (1.7 mM),  $\text{Na}_2\text{CO}_3$  (1.8 mM), and acetonitrile (23 vol%). The detection limit of  $\text{ClO}_4^-$  was 0.58  $\mu\text{M}$  (58  $\mu\text{g L}^{-1}$ ), calculated from a signal-to-noise ratio of 3. An LC-MS/MS system consisting of an HPLC system (Agilent 1100), an anion-exchange column (IonPac AS-21, Dionex), and a mass spectrometer (Micromass Quatro, Waters) was used to quantify  $\text{ClO}_4^-$  in the water sample from the man-made reflecting pond following fireworks display and its reaction solution. The detection limit of  $\text{ClO}_4^-$  was 0.20 nM (0.02  $\mu\text{g L}^{-1}$ )<sup>3</sup>.

## Results and discussion

Initially, we studied the decomposition of  $\text{ClO}_4^-$  in PHW in the absence of a metal additive. The densities of the liquid and gas phases of pure water at 300 °C, at which the two phases coexist, are reported to be 0.71214 and 0.046168  $\text{g mL}^{-1}$ , respectively<sup>11</sup>. These density values and the water amount (3.5 g) and the internal reactor volume (11 mL) in the present study indicate that the volumes of the liquid and gas phases at 300 °C, the highest temperature tested, were 4.5 and 6.5 mL, respectively. This fact demonstrated that the reactions proceeded in PHW. The effect of temperature on  $\text{ClO}_4^-$  decomposition, in the absence of a metal, is shown in Fig. 1; the reaction time was 6 h and the initial concentration of  $\text{ClO}_4^-$  was 103  $\mu\text{M}$ . The residues of  $\text{ClO}_4^-$  gradually decreased with increasing the temperature and  $\text{Cl}^-$  was detected in the reaction solution. However, the reactivity of  $\text{ClO}_4^-$  in PHW was considerably low: when the reaction was carried out at 300 °C, the highest temperature tested, 84% of the initial  $\text{ClO}_4^-$  remained, accompanied by the formation of a very small concentration of  $\text{Cl}^-$ , with a yield [(molar concentration of  $\text{Cl}^-$  formed) / (molar concentration of the initial  $\text{ClO}_4^-$ )] of 10%. The low yield reflects the high thermal and chemical stability of  $\text{ClO}_4^-$ . Total recovery of chlorine, i.e., the molar ratio of total chlorine in  $\text{Cl}^-$  formed and remaining  $\text{ClO}_4^-$  to total chlorine atoms in the initial  $\text{ClO}_4^-$  was 94%, indicating that  $\text{ClO}_4^-$  and  $\text{Cl}^-$  were virtually the only chlorinated species present in the reaction solution. Consistently, other chlorinated species such as  $\text{ClO}_3^-$  and  $\text{ClO}_2^-$  were not detected in the reaction solution, indicating that these two species are unstable in PHW.

To enhance the decomposition of  $\text{ClO}_4^-$  in PHW, we carried out reactions in the presence of a metal powder. The results are summarized in Table 1; the reaction was carried out at 150 °C for 6 h. In the absence of a metal (entry 1), most (99%) of the initial  $\text{ClO}_4^-$  (103  $\mu\text{M}$ ) remained, accompanied by a very small yield (3%) of  $\text{Cl}^-$ . Addition of aluminum did not enhance the formation of  $\text{Cl}^-$  (entry 2). Alternatively, addition of other metals clearly enhanced the decomposition of  $\text{ClO}_4^-$  to  $\text{Cl}^-$ , with an increasing order of,  $\text{Cu} < \text{Zn} < \text{Ni} \ll \text{Fe}$  (entries 3–6). The highest enhancement of decomposition of  $\text{ClO}_4^-$  to  $\text{Cl}^-$  was achieved by the addition of iron. After the reaction in PHW with iron for 6 h, no  $\text{ClO}_4^-$  was detected in the reaction solution, while  $\text{Cl}^-$  was formed, with a high yield (85%) (entry 6). The enhancement of the decomposition of  $\text{ClO}_4^-$  to  $\text{Cl}^-$  was not reflected by the reducing power of the metals, because the order of  $\text{ClO}_4^-$  reduction (or  $\text{Cl}^-$  increase) was different from the order of the redox potentials ( $E_0$ , V vs. NHE) of metals in the more negative direction of  $\text{Cu}/\text{Cu}^{2+}$  (0.34)  $<$   $\text{Ni}/\text{Ni}^{2+}$  (-0.26)  $<$   $\text{Fe}/\text{Fe}^{2+}$  (-0.44)  $<$

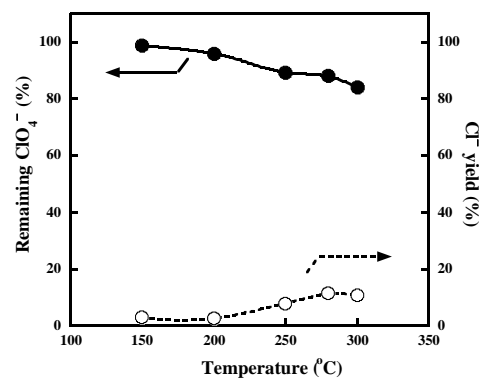


Fig. 1. Effect of temperature on the decomposition of perchlorate ( $\text{ClO}_4^-$ ) in pressurized hot water (PHW) in the absence of metal at a constant reaction time of 6 h<sup>10</sup>. An argon saturated aqueous solution (3.5 mL) of  $\text{ClO}_4^-$  (103  $\mu\text{M}$ ) was introduced in a sealed reactor, then the reactor temperature was raised between 150 and 300 °C.

$Zn/Zn^{2+}$  ( $-0.76$ ) <  $Al/Al^{3+}$  ( $-1.68$ ). This finding suggests that the reduction of  $ClO_4^-$  on metal surface is not a simple redox reaction. It appears that specific interaction between  $ClO_4^-$  and metal surface (such as adsorption) plays an important role in the decomposition of  $ClO_4^-$ . In each case,  $ClO_3^-$  and  $ClO_2^-$  were not detected in the reaction solution.

Table 1  
Decomposition of perchlorate ( $ClO_4^-$ ) in pressurized hot water (PHW) with and without metal additives <sup>a 10)</sup>

entry	Metal additive	Weight of metal additive (mg)	Particle size of metal additive ( $\mu m$ )	Initial $ClO_4^-$ concentration ( $\mu M$ )	Remaining $ClO_4^-$ (%)	$Cl^-$ yield (%)
1	none	–	–	103	99	3
2	Al	24.5	< 75	103	93	1
3	Cu	57.7	< 75	101	86	13
4	Zn	59.3	< 75	102	51	22
5	Ni	53.4	< 53	100	46	43
6	Fe	50.8	< 53	104	< 1 <sup>b</sup>	85 $\pm$ 1

<sup>a</sup> An argon saturated aqueous solution (3.5 mL) of  $ClO_4^-$  and metal powder (0.91 mmol) were introduced into the reactor under argon, and the reactor was heated to 150 °C for 6 h.

<sup>b</sup> Below the detection limit of ion chromatography.

Because the addition of iron powder led to the most efficient  $Cl^-$  formation among the metals tested, we further investigated the decomposition of  $ClO_4^-$  to  $Cl^-$  with iron by changing the reaction conditions. The reaction-time dependence of the residual  $ClO_4^-$  ratio and  $Cl^-$  yield in the reaction solution is shown in Fig. 2; the initial concentration of  $ClO_4^-$  was 104  $\mu M$  and the reaction temperature was 150 °C. The amount of  $ClO_4^-$  remaining in the solution decreased from 100 to 94% after addition of iron at 23 °C: 6% of the initial  $ClO_4^-$  was removed from the solution even before heating, with no  $Cl^-$  formed. This may be due to the adsorption of  $ClO_4^-$  on the iron surface. After heating, the concentration of  $ClO_4^-$  rapidly decreased with increasing reaction time, following pseudo-first-order-kinetics with a rate constant of 4.3  $h^{-1}$ , while  $Cl^-$  increased. After 1 h,  $ClO_4^-$  was not detected in the reaction solution. The formation of  $Cl^-$  showed saturation in 2 h, which indicates that the reaction was almost complete during this period, and the yield of  $Cl^-$  reached 85% after 6 h.

The effect of temperature on  $ClO_4^-$  decomposition in the presence of iron is shown in Fig. 3; the reaction time was 6 h and the initial concentration of  $ClO_4^-$  was 104  $\mu M$ . Raising the reaction temperature from 23 °C dramatically decreased the residual  $ClO_4^-$  and increased  $Cl^-$  yield. After the reaction at 80 °C for 6 h, 45% of the initial  $ClO_4^-$  remained, followed by a  $Cl^-$  yield of 46%.

The concentration of  $ClO_4^-$  decreased below the detection limit at 150 °C, and the  $Cl^-$  yield increased to a maximum (85%). Therefore, it was clear that the best reaction temperature for the decomposition of  $ClO_4^-$  to  $Cl^-$  induced by iron in the present study was 150 °C, at which temperature the reaction was almost complete in 2 h (Fig. 2).

We used perchlorate-contaminated water from a man-made reflecting pond following a fireworks display, to

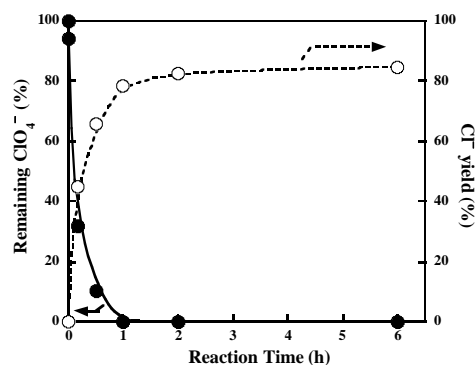


Fig. 2. Reaction-time dependence of the residual  $ClO_4^-$  ratio and the  $Cl^-$  yield<sup>10)</sup>. Iron powder (0.91 mmol) was added to an argon saturated aqueous solution (3.5 mL) of  $ClO_4^-$  (104  $\mu M$ ) under argon atmosphere, and the mixture in the sealed reactor was heated at 150 °C for 1–6 h. Two dots for  $ClO_4^-$  at time 0 correspond to the values obtained before (higher value) and after (lower value) addition of iron.

evaluate the efficiency of the developed method for the remediation of contaminated waters. This sample contained 5.22  $\mu\text{M}$  of  $\text{ClO}_4^-$  and much higher concentrations of  $\text{Cl}^-$  (472  $\mu\text{M}$ ) and  $\text{SO}_4^{2-}$  (130  $\mu\text{M}$ ), which might interfere with the decomposition of  $\text{ClO}_4^-$ . Therefore, we prolonged the reaction time to 18 h and increased the amount of iron to 1.82 mmol. Consequently, the concentration of  $\text{ClO}_4^-$  was dramatically reduced to  $0.03 \pm 0.01 \mu\text{M}$  after the reaction at 150  $^\circ\text{C}$ : 99% of the initial  $\text{ClO}_4^-$  was effectively removed from the water.

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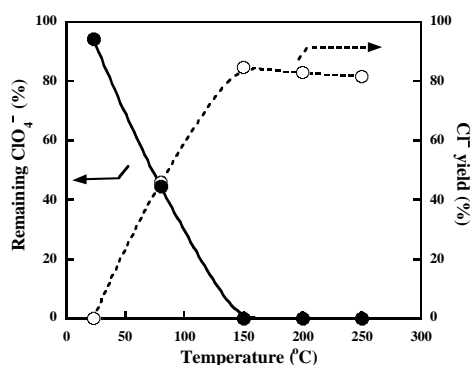


Fig. 3. Effect of temperature on the decomposition of  $\text{ClO}_4^-$  in PHW in the presence of iron at a constant reaction time of 6 h<sup>10</sup>. An argon saturated aqueous solution (3.5 mL) of  $\text{ClO}_4^-$  (104  $\mu\text{M}$ ) and iron powder (0.91 mmol; 50.8 mg, < 53  $\mu\text{m}$ ) were introduced in the sealed reactor under argon atmosphere, then the reactor temperature was raised between 80 and 250  $^\circ\text{C}$ .