Reaction of zero-valent magnesium with water: Potential applications in environmental remediation

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Abstract

This study examined the dissolution kinetics of granular zero-valent Mg (ZVMg) at pH 7 in water that was open to the atmosphere and buffered with 50 mM Na–MOPS. The oxidative dissolution of ZVMg was rapid; the initial amount of ZVMg (10–50 mg/L) dissolved completely within 200 min. The rate and extent of ZVMg dissolution was not affected by atmospheric oxygen. Although the oxidation of ZVMg is thermodynamically more feasible by dissolved oxygen or proton ions (H^+), the primary oxidants are water molecules. The initial rate of ZVMg dissolution obeys first order kinetics with respect to ZVMg concentration with an observed rate constant, $k_{Mg,7} = 1.05 \pm 0.06 \times 10^{-2} \, min^{-1}$. Model calculations using the rate constant perfectly predict the extent of ZVMg dissolution for an extended time period at lower $[Mg^0]_0$ but underestimate at 50 mg/L $[Mg^0]_0$. The offset is likely attributed to the rapid dissolution of ZVMg particles, which could cause a substantial increase in the specific surface area. As to the reactivity of Mg–water system, we suggest that the hydrated electron (e_{aq}^-), the most powerful reducing agent, would probably be the major reactive entity under neutral and alkaline conditions. In addition, we discuss briefly the factors affecting the rate and extent of the Mg–water reaction such as background electrolytes, ZVMg impurities, surface passivation, solution pH and temperature based on literature review.

1. INTRODUCTION

The applications of metallic Mg are remarkably far-reaching and have stimulated intense research efforts in diverse science and engineering fields. Magnesium alloys are utilized in the aerospace, weapon, automotive, and electronic device industries because of their low densities and potentially high specific strength as well as the abundance of Mg in seawater (e.g., Makar and Kruger, 1993; Song et al., 1997a; Zhang et al., 2008). However, the poor corrosion resistance of Mg due to its high intrinsic reactivity restricts its more wide-spread application (Baril et al., 2007; Song and Atrens, 2007). Hence, the reaction of Mg with water, which is the main process of Mg corrosion, has been of an important research subject to improve the resistance

in the fields of metallurgy and corrosion science. On the other hand, enhancement of the Mg–water reaction is beneficial in some chemical applications such as for heat or H_2 generation (Taub et al., 2002).

Likewise, unusually high reactivity of metallic Mg has led to investigations into the potential applications of Mg as a powerful reductant especially of organic contaminants (Morales et al., 2002a,b; Patel and Suresh, 2006, 2008; Agarwal et al., 2007; DeVor et al., 2009). Utilization of zero-valent Mg (ZVMg) for the treatments of contaminants is considered to have several potential advantages over using zero-valent iron (ZVI); (1) ZVMg ($E_{SHE}^0 = -2.37 \, V$) has a higher reduction potential than ZVI ($E_{SHE}^0 = -0.44 \, V$); (2) $Mg(OH)_2(s)$ is much more soluble than $Fe(OH)_3(s)$, thereby reducing passivation on ZVMg compared to ZVI; and (3) ZVMg can be applied under both aerobic and anaerobic conditions in contrast to ZVI, whose application is limited to anaerobic conditions, which is another advantage of ZVMg for sample handling and storage (Engelmann

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et al., 2001; Agarwal et al., 2007; Gautam and Suresh, 2007). Furthermore, the natural abundance and eco-friendly reaction product (Mg^{2+}) make ZVMg an attractive option in the contaminant treatment processes.

Despite the potential advantages of ZVMg, research of contaminant removal using ZVMg is rare. Previous studies deployed mostly bimetallic Mg systems with various metal catalysts primarily to treat recalcitrant organic contaminants. Bimetallic ZVMg systems have been successfully utilized to dehalogenate various chlorinated organic compounds such as DDT, PCB, and chlorinated phenols (e.g., Engelmann et al., 2001; Morales et al., 2002a; Agarwal et al., 2007; DeVor et al., 2009). As in the case for ZVI, Pd is the most common metal catalyst in ZVMg bimetallic systems. Without a catalyst, the efficiency of ZVMg alone for dechlorination is considerably reduced (Morales et al., 2002a,b; Agarwal et al., 2007) but is still higher than pure ZVI and comparable to that of Pd/Fe systems for removal of chlorinated phenols (Morales et al., 2002a). In most cases, hydrogenation is commonly thought to be the key process responsible for the reductive dechlorination in bimetallic systems. Recently, however, hydrogen atom (H·) has been postulated to be responsible for the primary reactivity of Fe-based (Cheng et al., 1997; Lin et al., 2004; Odziemkowski and Simpraga, 2004; Cwiertny et al., 2006, 2007) and Mg-based bimetallic systems (Patel and Suresh, 2006, 2008; De-Vor et al., 2009). Especially, Cwiertny et al. (2007) proposed that the extent of H· absorption in the metal catalyst determines the reactivity of Fe-based bimetallic systems.

Reactive intermediate species of Mg–water reactions have been more extensively discussed on the processes of Mg corrosion. One of the main interests is to understand the mechanism responsible for excess H_2 evolution from Mg electrodes; H_2 production increases with increasing anodic potential, which is a unique phenomenon of Mg anodic dissolution. Four hypotheses have been proposed to explain this phenomenon, which is referred to as the negative difference effect (NDE); (1) the partially protective film model; (2) the hydride model; (3) the monovalent Mg (Mg^+) model; and (4) the undermining second phase particle model (Song et al., 1997b and references therein). Among the suggested hypotheses, it is widely presumed that anodic dissolution of a Mg electrode generates highly reactive mono-valent Mg (Mg^+) as an intermediate, which in turn is thought to produce excess H_2 (NDE) by reducing water (Petty et al., 1954; Song et al., 1997b; Baril et al., 2007; Song and Atrens, 2007). If this is the case, the Mg^+ intermediate would also be a suitable candidate for the primary reductant of pure or bimetallic Mg systems. On the other hand, Taub et al. (2002) examined the kinetics of 5 mol% Fe-activated Mg dissolution in different concentrations of NaCl electrolyte solution and proposed a potential mechanism for H_2 production from the Mg–water reaction by evaluating the effects of diverse solutes on the H_2 yield. They found that the effects of added solutes on the generation of H_2 are remarkably consistent with those in the radiolysis of water and suggested that hydrated electron (e_{aq}^-) is the principal precursor of H_2 production. The vast amounts of information available about Mg–water reactions in the corrosion science and chemistry literature, however, have been scar-

cely exploited to improve our understanding of mechanistic remediation processes using ZVMg. Moreover, to the best of our knowledge, the reaction of ZVMg with water has not been explicitly examined in the context of environmental geochemistry. In this paper, we assess the dissolution kinetics of ZVMg in water under neutral pH conditions, review the results available in the literature concerning Mg–water reactions, and discuss the reactivity and potential applications of ZVMg in environmental remediation.

2. MATERIALS AND METHODS

2.1. Reagents

The material used in this study was granular Mg obtained from Duksan Purechemical Co. The purity was 99.68% (0.05% Si, 0.02% Cu, 0.05% Fe, 0.05% Al, 0.10% Mn, 0.05% Zn). All other chemicals were reagent grade or better and were used without further purification: NaCl (Showa), NaOH (Junsei), HCl (Aldrich), and MOPS sodium salt ($C_7H_{14}NNaO_4S$; Aldrich). Solutions were prepared with deionized water purified using a reverse osmosis and ultrapure water system ($\geqslant 18.0$ MΩ-cm).

2.2. Stability of the solution pH

In this study, all experiments were conducted at pH 7. Prior to any experiments, the pH stability of solutions containing 10–500 mg/L ZVMg was examined at various concentrations of MOPS buffer. Inorganic buffers such as carbonate or phosphate were avoided due to their potential effects on the rate of ZVMg dissolution as discussed later in Section 3.3.1. First, an appropriate amount of MOPS sodium salt was dissolved in 100 mL of deionized water to prepare 10, 50, 100, or 500 mM MOPS solution in a 250 mL polypropylene beaker. The pH of each solution was adjusted to 7.00 by adding small amounts of acid or base (1.0 or 5.0 M HCl or NaOH). Subsequently, 1.0–50.0 mg ZVMg was added to each solution, which was stirred with a Teflon stir bar on a magnetic stirring plate, and the solution pH was monitored up to 1200 min (Fig. 1). With 10 mM MOPS, only the solution containing 10 mg/L ZVMg was stable at pH 7.03 ± 0.04 for 1140 min. In contrast, for solutions containing higher ZVMg concentrations, the pH increased with time and reached 7.50, 8.40, and 10.19 at 25, 50, and 500 mg/L ZVMg, respectively, after 1140 min. For 50 mM MOPS solution, the pH stabilized at 7.01 ± 0.04 at $\leqslant 50$ mg/L ZVMg for 870 min but increased to 9.86 at 500 mg/L ZVMg for the same time period. At 500 mg/L ZVMg, the solution pH still increased to 8.79 and 7.20, even with 100 and 500 mM MOPS, respectively, for ca. 500 min. Consequently, the maximum ZVMg concentration employed in this study was 50 mg/L, and the pH of every solution was amended with 50 mM MOPS as a buffer for further experiments.

2.3. Oxidative dissolution of ZVMg

Batch experiments for ZVMg dissolution were conducted with varying amounts of ZVMg in 50 mM MOPS