Chapter 16

Titanium Catalyzed Perchlorate Reduction and Applications

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**INTRODUCTION**

Catalyzed chemical and electrochemical techniques to reduce perchlorate (ClO$_4^-$) to chloride are possible, although their direct use in drinking water treatment has been very limited. This limited use is partly due to the introduction of chemicals; chemical oxidation byproducts; and the slow reduction kinetics of perchlorate as a result of the high activation energy required, as discussed in Chapter 1. Common reductants such as zero-valent iron metals, dithionite, sulfite, and thiosulfate do not react with ClO$_4^-$ ions at any observable rate at ambient temperature and pressure. However, perchlorate has been reported to have been reduced by several transition metal ions such as titanium(III), vanadium(II)/(III), molybdenum(III), and ruthenium(II) and iron(II) at an elevated temperature in aqueous solution. Although electrochemical technologies are well established for other industries (e.g., electroplating of metals and electrolysis of brines), they have not yet found direct application in drinking water treatment, perhaps because of the relatively high capital and energy costs for degrading contaminants at low concentrations.

However, the catalyzed electrochemical technique may well be suited for degrading ClO$_4^-$ in small waste streams such as concentrated brines used for regenerating spent anion-exchange resins. In particular, a novel application of a catalyzed electrochemical technique has recently been reported to directly reduce ClO$_4^-$ sorbed on a spent ion-exchange resin bed, thereby regenerating the resin as illustrated in Figure 1. In this case, a typical fixed resin bed is regenerated by catalyzed electrochemical reduction of ClO$_4^-$ sorbed on the resin in a recirculation electrochemical cell. Reduced Ti(III) serves as a reducing agent and, once it is oxidized as Ti(IV), it is re-reduced at the cathode. This technique essentially eliminates the generation of secondary wastes because a recycle mode is used. It is particularly suited for
destroying perchlorate and regenerating those highly selective resins, thereby significantly decreasing both the operational and capital costs by ion exchange. This chapter will cover both the theoretical and practical aspects of titanium-catalyzed electrochemical reduction of perchlorate and its potential applications for water treatment.

PERCHLORATE REDUCTION KINETICS BY Ti(III)

Literature reviews indicate that ClO$_4^-$ reduction can occur only when it is accompanied by an oxygen atom transfer reaction$^{1,2}$ because the perchlorate anion has no low-lying electronic energy levels available to accept an electron in a single electron transfer reaction. This explains why only certain transition metal ions such as Ti(III), V(III), V(II), Mo(III), Re(V), and Ru(II) are capable of reducing ClO$_4^-$, because they can accept an oxygen atom from perchlorate, or the redox reaction is formally an oxygen atom transfer reaction. The reaction may be written as either a one- or a two-electron transfer process depending on the characteristics of the reducing agent.

$$\text{ClO}_4^- + e^- \rightarrow \text{ClO}_3^- + \text{O}_2^2.$$  \hfill (1)