Ligand-promoted dissolution of serpentine in ultramafic nickel ores

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ABSTRACT

The ligands catechol, citrate, EDTA, oxalate and tiron were investigated for their ability to improve the dissolution of serpentine in ultramafic nickel ores at neutral to alkaline pH to enhance mineral carbon sequestration. It is desirable to leach magnesium from serpentine in ores at neutral to alkaline pH so that leaching and carbonation can be conducted at the same pH value, and ultimately so that the reagent requirements of mineral carbon sequestration can be reduced. Both solution modeling and experimental work were conducted. The solution modeling revealed that each of the ligands studied is able to enhance the solubility of magnesium at the desired pH, with the order of effectiveness being EDTA > tiron > citrate > catechol > oxalate. Experimentally it was shown that the ligands studied could improve both the total amount and rate of magnesium leaching from ultramafic nickel ores. The order of ligand effectiveness based on the experimental work for the Pipe ore was EDTA ⩾ tiron > catechol > oxalate ⩾ citrate. For the OK ore, the order was tiron > EDTA = catechol > oxalate > citrate. Overall, the ligands studied in this work, particularly EDTA, tiron, and catechol, appear promising for enhancing the dissolution of serpentine in ultramafic nickel ores at neutral to alkaline pH.

1. Introduction

The rate limiting step during aqueous mineral carbon sequestration (MCS) is the dissolution of the silicate mineral (Krevor and Lackner, 2011). To overcome the slow dissolution kinetics, a number of extraction agents have been investigated for use in indirect aqueous MCS schemes, including acids and ammonium salts (Baldyga et al., 2010; Kakizawa et al., 2001; Kodama et al., 2008; Park and Fan, 2004; Pundsack, 1967; Teir et al., 2007). Indirect aqueous MCS involves the extraction of reactive components (Mg^{2+}, Ca^{2+}) from silicate minerals, followed by the reaction of the extracted components with CO_2 in the aqueous phase (Bobicki et al., 2012). In both acid and ammonia extraction, a proton is used to liberate the alkaline earth metal ion from the silicate matrix. It is believed that lone pairs of electrons present on oxygen atoms in the silicate structure undergo protonation as the proton concentration increases. The protonation of the oxygen atoms polarizes and weakens the Mg–O–Si bonds, enabling the release of magnesium ions into solution, as shown by reaction 1 (Alexander et al., 2007; Oelkers, 2001; Stumm, 1992).
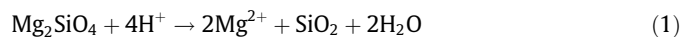
$$Mg_2SiO_4 + 4H^+ \rightarrow 2Mg^{2+} + SiO_2 + 2H_2O \qquad (1)$$

Although indirect aqueous MCS processes utilizing proton-promoted dissolution can achieve high carbonate conversions under relatively mild processing conditions, the chemical reagent requirements can be prohibitively high as chemicals must be added both for the extraction of the reactive component, and for pH adjustment after leaching for carbonate precipitation (Teir et al., 2009).

Recently, interest in developing a chemically-enhanced direct aqueous MCS process has arisen (Krevor and Lackner, 2011; Bonfils et al., 2012). In the proposed process, ligands are used to aid in the dissolution of the silicate mineral and there is no separation of the extracted magnesium and the remaining solids prior to carbonation. In fact, the ligands continue to aid mineral dissolution during carbonation. Ligand-enhanced dissolution of silicate minerals for MCS is particularly interesting because the chelating effects can occur at neutral to alkaline pH. As a result, the consumption of large quantities of acids and bases is not required, as it would be in the classic pH swing process (Krevor and Lackner, 2011; Prigiobbe and Mazzotti, 2011; Park et al., 2003; Wogelius and Walther, 1991). If the dissolution of silicate minerals could be promoted at a pH value conducive to carbonate precipitation, the chemical cost of aqueous MCS processes could be reduced. Additional benefits of using ligands to enhance direct MCS processes include the potential for the recycling of the leach solution after carbonation, and that ligands could prevent the re-precipitation of iron during

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leaching, which would otherwise inhibit dissolution of silicate minerals (Park et al., 2003).

Ligands, or chelating agents, aid in mineral dissolution by specifically adsorbing on mineral surfaces and forming highly soluble complexes with metal ions (e.g. magnesium in serpentine). The formation of ligand–metal complexes at the mineral surface shifts the electron density toward the metal ion, which destabilizes the Me–O lattice bonds and facilitates the detachment of metal ions into solution (Stumm, 1992). Ligands also enhance the dissolution of minerals by forming complexes with leached ions in solution, thus, lowering the apparent solubilization of the mineral (Prigiobbe and Mazzotti, 2011). The ligand (oxalate shown) promoted dissolution of alumina is shown in Fig. 1.

A number of ligands have been shown to improve the dissolution of silicates in nature, including oxalate, citrate, diphenols, and hydroxycarboxylic acids (Stumm, 1992). In the laboratory, acetate, ascorbate, citrate, EDTA, potassium hydrogen phthalate, oxalate and tannate have been shown to enhance the dissolution of olivine (Grandstaff, 1986; Hänchen et al., 2006; Olsen and Rimstidt, 2008; Prigiobbe and Mazzotti, 2011; Wogelius and Walther, 1991). Similarly, it has been demonstrated that catechol, citrate, EDTA and oxalate improve the dissolution of serpentine (Bales and Morgan, 1985; Krevor and Lackner, 2011; Park and Fan, 2004). To date, ligands have primarily been investigated for the dissolution of silicate minerals at acidic to neutral pH. However, carbonation under the same conditions has not resulted in the complete conversion of the leached magnesium to magnesium carbonate (Krevor and Lackner, 2011; Park and Fan, 2004). To preferentially precipitate the leached magnesium as magnesium carbonate, an adjustment of leachate to pH 9 or 10 has been required, just as when acid extraction is used in indirect aqueous MCS schemes (Park and Fan, 2004). Thus, the effectiveness of ligands to improve the leaching of magnesium from silicate minerals at neutral to alkaline pH is of particular interest for MCS.

The objective of this paper is to investigate the effectiveness of five different ligands for improving the leaching of magnesium from serpentine in ultramafic nickel ores at neutral to alkaline pH and room temperature. Solution modeling was used to determine the capacity of the ligands to enhance the solubility of Mg across the pH range. The ability of the ligands to enhance the dissolution of Mg from ultramafic ores was examined experimentally at pH 7 and 10. The effect of ligand concentration on total Mg leached was also examined. Subsequently, the effect of the ligands on Mg leaching rates was investigated at several ligand concentrations, again at pH 7 and pH 10. The ligands tested include catechol ($C_6H_6O_2$), citrate ($C_6H_5O_7^{3-}$), ethylenediaminetetraacetic acid (EDTA, $C_{10}H_{16}N_2O_8$), oxalate ($C_2O_4^{2-}$) and tiron ($C_6H_6O_8S_2$) (Fig. 2). The ligands were selected based on the strength of their stability constants and their affinity for magnesium (Table 1). Ultramafic nickel ores were selected as feedstock in this work as the waste material produced by nickel extraction is primarily serpentine, a
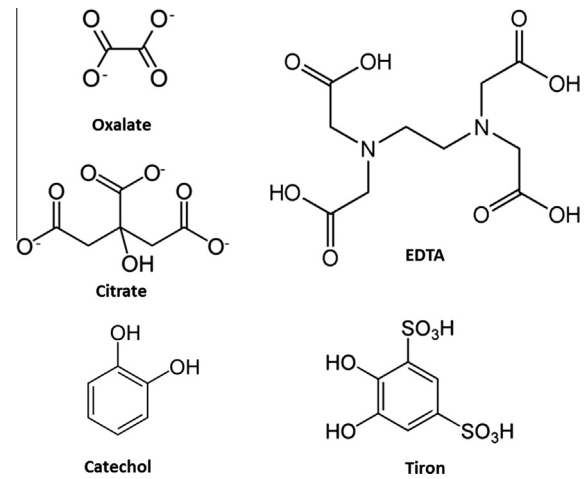
Fig. 2. Ligands selected for enhancing the leaching of magnesium from serpentine in ultramafic nickel ores.

Table 1
Equilibrium constants used in speciation modeling at temperature of 25 °C and ionic strength 0.1 unless otherwise noted. *Note:* Cat = catechol ($C_6H_4O_2^{2-}$), Cit = citrate ($C_6H_5O_7^{3-}$), EDTA = ethylenediaminetetraacetic acid ($C_{10}H_{12}N_2O_8^{4-}$), Ox = oxalate ($C_2O_4^{2-}$), Tiron = $C_6H_2O_8S_4^{2-}$.

Reaction	pK	Reference
$H^+ + Cat^{2-} \leftrightarrow HCat^-$	−13.0	1
$H^+ + HCat^- \leftrightarrow H_2Cat$	−9.23	1
$Mg^{2+} + Cat^{2-} \leftrightarrow MgCat$	−5.7[a]	1
$H^+ + Cit^{3-} \leftrightarrow HCit^{2-}$	−5.69	1
$H^+ + HCit^{2-} \leftrightarrow H_2Cit^-$	−4.35	1
$H^+ + H_2Cit^- \leftrightarrow H_3Cit$	−2.87	1
$Mg^{2+} + Cit^{3-} \leftrightarrow MgCit^-$	−3.37	1
$Mg^{2+} + HCit^{2-} \leftrightarrow MgHCit$	−1.92	1
$Mg^{2+} + H_2Cit^- \leftrightarrow MgH_2Cit^+$	−0.84[b]	1
$H^+ + EDTA^{4-} \leftrightarrow HEDTA^{3-}$	−10.17	1
$H^+ + HEDTA^{3-} \leftrightarrow H_2EDTA^{2-}$	−6.11	1
$H^+ + H_2EDTA^{2-} \leftrightarrow H_3EDTA^-$	−2.68	1
$H^+ + H_3EDTA^- \leftrightarrow H_4EDTA$	−2.0	1
$H^+ + H_4EDTA \leftrightarrow H_5EDTA^+$	−1.5	1
$H^+ + H_5EDTA^+ \leftrightarrow H_6EDTA^{2+}$	0	1
$Mg^{2+} + EDTA^{4-} \leftrightarrow MgEDTA^{2-}$	−8.83	1
$H^+ + MgEDTA^{2-} \leftrightarrow MgHEDTA^-$	−3.85	1
$H^+ + Ox^{2-} \leftrightarrow HOx^-$	−3.82	1
$H^+ + HOx^- \leftrightarrow H_2Ox$	−1.04	1
$Mg^{2+} + Ox^{2-} \leftrightarrow MgOx$	−2.76[c]	1
$Mg^{2+} + 2Ox^{2-} \leftrightarrow Mg(Ox)_2^{2-}$	−4.24	1
$H^+ + Tiron^{4-} \leftrightarrow HTiron^{3-}$	−12.5	1
$H^+ + HTiron^{3-} \leftrightarrow H_2Tiron^{2-}$	−7.61	1
$Mg^{2+} + Tiron^{4-} \leftrightarrow MgTiron^{2-}$	−6.86	1
$Mg^{2+} + HTiron^{3-} \leftrightarrow MgHTiron^-$	−1.98	1
$Mg^{2+} + OH^- \leftrightarrow MgOH^+$	−2.57	2
$Mg^{2+} + 2OH^- \leftrightarrow Mg(OH)_{2(aq)}$	−5.81	2
$Mg(OH)_{2(aq)} \leftrightarrow Mg(OH)_{2(s)}$	−2.67	2

Ref. [1] by Smith and Martell (1975); and Ref. [2] by Prédali and Cases (1973).
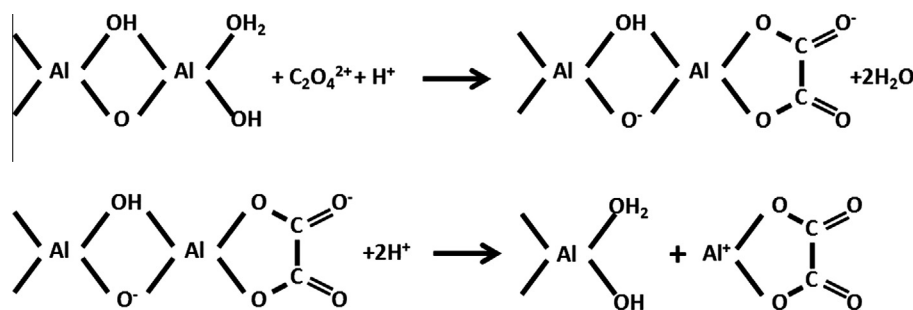[a] 30 °C, 0.1.
[b] 25 °C, 1.0.
[c] 20 °C, 0.1.

Fig. 1. Illustration of ligand-promoted dissolution.