



Silicate, phosphate and carbonate mineral dissolution behaviour in the presence of organic acids: A review



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ABSTRACT

Researchers in the field of geoscience have identified several effects on the stability of the surrounding minerals caused by naturally occurring solution species. Organic acids and their conjugate salts have been shown to provide significant influence on a wide range of minerals, generally increasing elemental mobility and aiding in solubilising the solid matrix. Their ability to complex elemental and molecular species, presents interesting opportunities in manipulating systems to achieve outcomes that are otherwise not thermodynamically favoured. Such properties form the basis of some analytical techniques such as the toxicity characteristic leaching procedure (TCLP) used in environmental assessment of waste product stability and the acidified ammonium oxalate (AAO) process used to selectively dissolve poorly crystalline iron oxide phases.

These characteristics also present the opportunity for use of these species to aid in industrial dissolution of value-containing minerals (extractive metallurgy). Such an approach provides the basis for the current review. The literature has been reviewed to identify organic acids – particularly low molecular weight organic acids (LMWOAs) – that significantly aid dissolution of relevant minerals, trends in their behaviour and fundamental explanations for these observations. It is also of interest to find evidence that these acids may improve selectivity in a hydrometallurgical application. This review is limited to silicate, carbonate and phosphate minerals as they represent the information relevant to the ongoing research.

Formic and acetic acids had the greatest impact on minerals composed of group I and II elements, while citric, oxalic, EDTA and salicylic acids represent the most promising options for transition metal and lanthanide-based minerals. The variation between the effect of the acids and a degree of the selective nature of their effect can be attributed to differences in the stability of the metal-ligand complex formed. pH plays a highly significant role, assisting the dissolution through, altering the dissociation of the acids, modifying the surface charge of the mineral, acid attack, maintaining the solubility of other dissolved ions and/or altering the mechanism involved. The crystal structure and secondary reactions occurring with other constituents in the mineral alter their amenability to dissolution in organic acids.

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1. Introduction

Organic acids are common, naturally occurring compounds, distinguished by the presence of the carboxylate (COOH) functional group. These range from very simple molecules such as formic acid (CHOOH) found in many ant species, through to DNA, the blueprint of complex life. LMWOA is a somewhat subjective term as the spectrum of molecule sizes is so great and each application may have a different perspective on what constitutes low molecular weight species. For the purpose of this paper the term includes aliphatic and aromatic compounds with 1–3 carboxylic acid functional groups.

1.1. Organic acids in geochemistry

The relationship between LMWOAs and mineral surfaces has been studied for several decades and is an important geochemical process (Wei et al., 2011). LMWOAs are commonly present in rhizosphere soils and distinctively found in the layer next to the soil-root interface (Kong et al., 2014). According to Lines-Kelly (2005), “the rhizosphere is the zone of soil surrounding a plant root where the biology and chemistry of the soil are influenced by the root”. These acids are created mainly by the decomposition of plant root systems, fungi residues and other organic material (Wang et al., 2005). An example are the prokaryotes, which are the first land-colonising organisms, which primarily create aliphatic acids and, to a lesser degree, aromatic compounds (Neaman et al., 2005). The structures of some common aliphatic and aromatic acids are given in Figs. 1 and 2.

Organic acids such as fulvic and humic acids, which are present in geological weathering systems, break down minerals to create metallo-organic chelates (Huang and Keller, 1972). Furthermore, organic acids (such as oxalic and citric acid) play an important role in many processes in the rhizosphere, i.e. metal detoxification and mineral weathering. They have also shown an ability to influence

geochemical processes such as concentration of elements, transportation and dissolution (Kiang and Huang, 1972).

Mineral weathering may be increased by organic acids and their anions (conjugate bases) (Drever and Stillings, 1997; Wang et al., 2005). The presence of carbonyl and hydroxyl functional groups in the organic acids structure allows the creation of complexes with elements in the soil (Kong et al., 2014). Mineral weathering by organic acids can be explained by at least three factors: (a) changing the speciation of ions in solution; (b) influencing the solution saturation with respect to the mineral; and (c) perturbing the dissolution reaction far from equilibrium (Drever and Stillings, 1997).

1.2. Applications in extractive metallurgy

It has been established that organic acids and their conjugate bases can be of great value in the minerals industry. One of the United States Environmental Protection Agency's (EPA) key tests for assessing the stability of toxic elements in waste material (TCLP) (EPA, 1992) contains acetic acid as a buffering agent. This test is used to determine the ability of toxic components including arsenic, lead, mercury, etc. to be released upon storage of waste products in or near natural systems. Also the acidified ammonium oxalate (AAO) (Smith, 1994) procedure for selectively dissolving amorphous and nanocrystalline iron oxides and hydroxides is a useful characterisation technique.

There are also examples of research evaluating the potential of organic acids for direct employment in mineral processing applications. The well-established complexing properties of these species have inspired research into a multitude of applications. This carries on from a significant history of complexation reactions in the extraction stage of metallurgy including the use of cyanide in gold leaching, employed since the 1890s, and ammonia in nickel processing (Caron process), established in the 1950s.

Nickel laterites are oxide ores generally with low nickel contents dispersed throughout the gangue minerals, these are difficult to treat and represent up to the 70% of known nickel reserves (Ntloyakhumo, 2008). The author used oxalic acid to leach iron selectively over nickel as a method of upgrading the ore and releasing trapped value. As they are not significantly upgraded via physical separation or flotation, a method of beneficiating nickel laterites ores before leaching, is highly important to improve the economics of the process. A similar study involved using citric and oxalic acids sequentially to selectively remove the various components of interest (Ni, Co and Fe) (Kursunoglu and Kaya, 2015).

A range of other studies have investigated the use of organic acids in extraction, (Fischman and Dixon, 2009) showed the value of using citrate as a complexing agent for iron in the ammoniacal leaching of awaruite (Ni₃Fe). Without citrate dissolved iron would reprecipitate as a hydroxide on the mineral surface forming a passive barrier to leaching. Li et al. (2015) displayed that a high proportion (>95%) of lithium and cobalt could be leached from spent

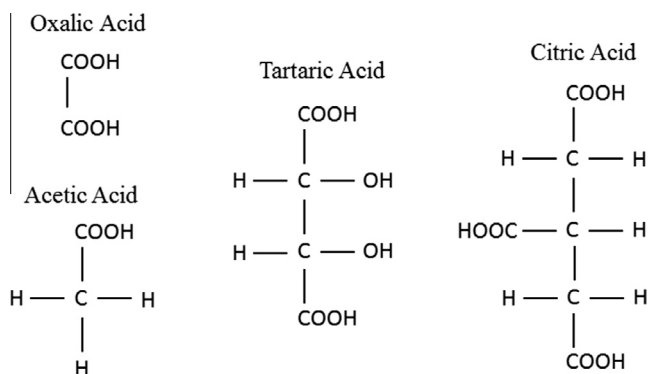


Fig. 1. Chemical structure of some common aliphatic acids.

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