



Utilization efficiency of lime consumption during magnesium sulfate precipitation



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ABSTRACT

In this study, the utilization efficiency of two quicklimes and their respective slaked lime slurry (milk of lime) products were evaluated using the precipitation of magnesium sulfate as a model system. Magnesium was selected because of its abundant presence in hydrometallurgical processing solutions and mineral processing slurries, where it is often the main buffering and lime consuming element at pH levels above 9. Lime, also called quicklime, purity is often measured in terms of available CaO percentage, CaO(avail%), the active component. The purpose of this investigation was to evaluate the validity and suitability of this commonly used industrial metric for the target application reaction. Two samples with CaO(avail%) of 93 and 80% w/w were used, in dry quicklime and slaked formats, as magnesium precipitation reagents. Utilization efficiencies were compared and found to differ significantly, depending on the original quicklime reagent and format of their respective slaked lime products. Utilization efficiency was defined as the mass portion of the quicklime that participates in the target application and was calculated for both slaked lime and quicklime reagent formats to facilitate comparisons. The main conclusion was that the CaO(avail%) metric was a very poor predictor of reagent utilization efficiency of slaked lime. Although the CaO(avail%) of quicklime, provides the theoretical amount of potential active reagent, slaked lime Ca(OH)₂ particle size was found to have a greater influence on utilization efficiency. Utilization efficiencies were found to range from 34 to 89% for slaked limes with median Ca(OH)₂ particle sizes of 67 and 5 μm respectively. Precipitate coating effects on larger Ca(OH)₂ particles were observed, leading to the occlusion of unreacted Ca(OH)₂ particles. This coating mechanism is proposed as a potential reason for reduced utilization efficiency of poor quality slaked lime with a significant portion of large Ca(OH)₂ particles. The findings demonstrate the potential error of assessing industrial slaked lime performance, based on lime CaO (avail%) alone. It is argued that industrial selection and assessment of lime sources, should instead be assessed by determining utilization efficiency in laboratory approximation tests of the target reactions or, at least, by industrial evaluation of slaked lime particle size distribution.

1. Introduction

In this study, the utilization efficiency of two quicklimes and their respective slaked lime slurry products were evaluated using the precipitation of magnesium hydroxide from magnesium sulfate as a model system. Magnesium was chosen because of its abundant occurrence in hydrometallurgical process solutions, originating from its ubiquitous presence in gangue minerals (Mbaya et al., 2013) and naturally occurring water, often used as industrial process water. Seawater and even hypersaline water, is increasingly being used in metallurgical processing, with Mg concentrations ranging from 1.3 to 13 g L⁻¹ (Whittington et al., 2003) depending on the amount of Mg present in the ores/minerals. Many base metal and refractory gold hydrometallurgical processes consume, or generate, sulfuric acid in an initial

leaching step (Mbaya et al., 2013; Steemson and Smith, 2009; Whyte et al., 2001; McDonald and Whittington, 2008) resulting in the dissolution of magnesium. This is particularly pronounced in saprolitic nickel laterite processing (Karidakis et al., 2005). In some laterite processing circuits, magnesium is also added as a precipitation reagent, in the form of MgO, to achieve mixed hydroxide precipitation of nickel and cobalt (Willis, 2007). Unlike iron and aluminium, magnesium cannot be precipitated from solution in acidic media with relatively inexpensive calcium carbonate reagent (Hammarstrom et al., 2003), in the form of limestone. Magnesium precipitation in sulfate systems starts at pH 9 and is practically complete (in the context of industrial metallurgical processing) by pH 10.5, i.e. residual concentration of 200 mg L⁻¹ conditions, however, often require pH control levels higher than the precipitation pH of magnesium. In gold processing, for

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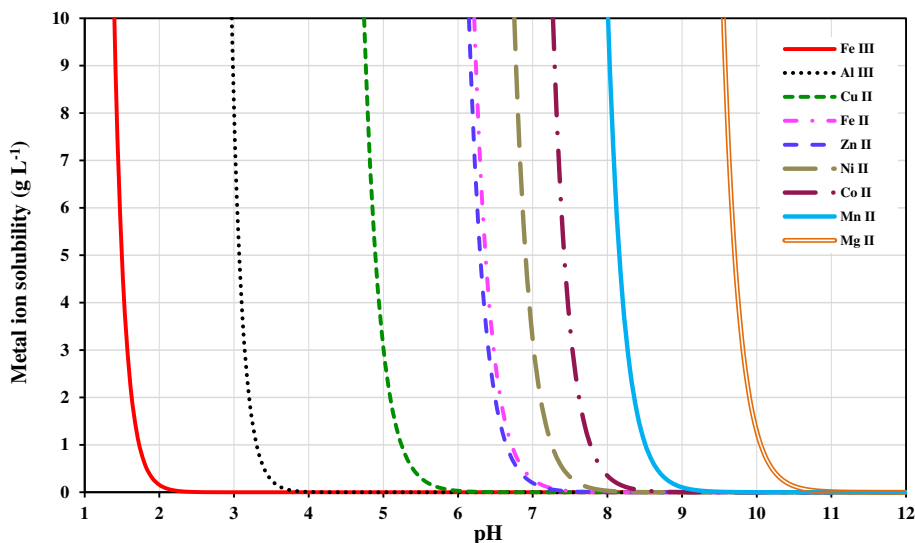


Fig. 1. Solubility of different non-ferrous metal hydroxides in sulfate media, based on solubility product data from this study, for Mg, and literature (Lide, 2002) for other elements.

example, cyanide leaching occurs at pH levels above 10 to ensure cyanide is maintained substantially in the CN^- rather than HCN form (Parga et al., 2012). Copper flotation processes are often also controlled at pH levels exceeding 9, to induce the selective depression of pyrite over copper sulfide minerals (Haga et al., 2012). Attaining these process pH set points requires increasing the pH, often with slaked lime (Zinck and Griffith, 2005), through the precipitation thresholds of various contained dissolved elements (Fig. 1) before reaching the pH buffering effect of the magnesium hydroxide precipitation reaction, where it plays a significant role because of its abundance in many circuits.

Environmental discharge limits for dissolved metal ions, may also impact on the extent of magnesium precipitation required. Hydrometallurgical effluents, for example, often have a strict discharge limit for Mn (Brunet and Artignan, 2006) which impacts on lime consumption because of the buffering effect of Mg. Achieving a 5 mg L^{-1} discharge threshold for manganese (as Mn(II)) in a process solution containing 15 g L^{-1} of Mg, for example (Stemson and Smith, 2009), will require a pH of approximately 9.66 and impose the co-precipitation of Mg to reduce its concentration to 6.1 g L^{-1} as illustrated in the Fig. 2. The solubility products for $\text{Mg}(\text{OH})_2$ and $\text{Mn}(\text{OH})_2$ used for calculating values shown in Fig. 2, were 5.28×10^{-10} (based on data from this study) and 1.90×10^{-13} (Lide, 2002) respectively. This phenomenon is particularly relevant for nickel laterite ores with high

concentrations of Mn (Watling et al., 2001). Although a relatively small amount of $\text{Ca}(\text{OH})_2$ may be required directly for Mn precipitation, the pH level required to achieve strict discharge limit targets imposes significant Mg co-precipitation effects, and therefore lime consumption. This effect may be reduced by using oxidation methods to convert Mn (II) to Mn(IV), which precipitates at significantly lower pH values than Mn(II). A commonly used oxidation technique is to sparge with SO_2 /air mixtures, however, this may further contribute to lime consumption due to the reaction of dissolved SO_2 with $\text{Ca}(\text{OH})_2$ (Zhang et al., 2000).

The most commonly used alkaline agents at pH levels above 6 are: lime (CaO), sodium hydroxide (NaOH) and magnesium oxide (MgO) of which lime is the lowest cost and, therefore, most frequently used to precipitate various metals ions from solution. The use of lime also has the advantage of removing sulfates from solution in the form of gypsum precipitates (Deng et al., 2013). The higher cost of MgO and NaOH , limits their applications to scenarios where gypsum co-precipitation is undesirable (White, 2009).

The common use of lime as pH adjustment and precipitation reagent makes it an important operational cost factor where high neutralization or precipitation duties are required. Lime utilization efficiency, together with price, is a determining factor of total lime cost. The accurate estimation of lime utilization efficiency is, therefore, an important industrial decision-making metric. In this context, “Utilization Efficiency” (typically below 90%) is defined as the mass proportion of the lime reagent that participates in the target application, i.e. the portion that effectively reacts as pure CaO . This definition of utilization efficiency is used because lime is mainly consumed and traded on a total mass basis in the base metal and gold metallurgical processing industry. Lime, also called quicklime, purity is often measured in terms of available CaO percentage (AFNOR, 2010, 2012; Australian Standard, 2016), hereafter abbreviated as $\text{CaO}(\text{avail}\%)$. This metric, however, does not give an indication of the utilization efficiency within the intended application. It is important to note that CaO does not directly react in the target reaction. Instead, CaO exothermically reacts with water to form slightly soluble $\text{Ca}(\text{OH})_2$ particles, which is the active reagent component (Oates, 2008). As consumption reactions of soluble $\text{Ca}(\text{OH})_2$ (or more precisely Ca^{2+} and OH^-) proceed, the solid $\text{Ca}(\text{OH})_2$ particles continuously dissolve to meet the reaction demand (Giles et al., 1993). It is, therefore, the properties of $\text{Ca}(\text{OH})_2$ particles that determine the ultimate utilization efficiency (Oates, 2008). “Utilization Efficiency” as defined in this context, encompasses the properties of the original lime reagent and all subsequent conversions and inefficiencies that ultimately result in the extent of $\text{Ca}(\text{OH})_2$ consumption in the target application within the available kinetic timeframe (Fig. 3).

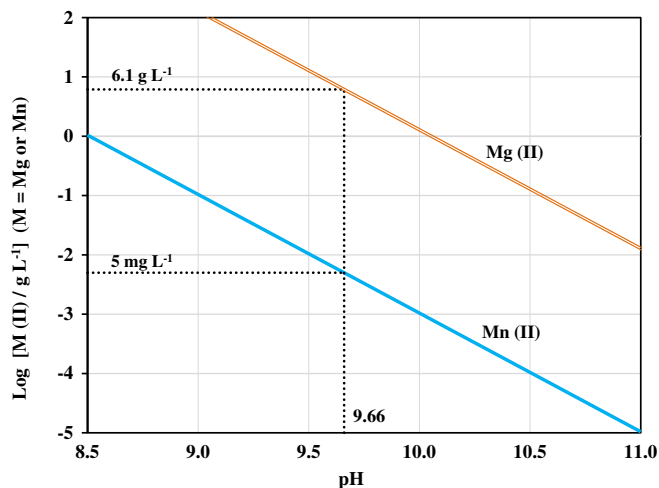


Fig. 2. Calculated magnesium and manganese hydroxides solubility values, as a function of pH.

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