Minerals Engineering 39 (2012) 39–44

Contents lists available at SciVerse ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

Stability of sodium polyphosphate dispersants in mineral processing applications

Saeed Farrokhpay *, Gayle E. Morris [1], Leanne G. Britcher

Ian Wark Research Institute, University of South Australia, Mawson Lakes, SA 5095, Australia

ARTICLE INFO

Article history:
Received 8 May 2012
Accepted 11 July 2012
Available online 4 October 2012

Keywords:
Polyphosphate
Calgon
Dispersion stability
Suspension rheology

ABSTRACT

Polyphosphates are commonly used industrially to provide electrostatic stabilisation to mineral and material suspensions. Polyphosphate solutions however have shown instability under processing conditions such as high temperature and acidic pH which may lead to a reduction in dispersion properties when added to mineral or material suspensions.

In this study the influence of pH, temperature and divalent cation concentration pre-treatment on polyphosphate dispersion properties is reported. Dispersion properties are determined using rheological suspension analysis. The suspensions investigated are material-based model systems of titania pigment and high purity boehmite. Infrared spectroscopy studies of polyphosphate solutions were undertaken to directly investigate the polyphosphate structure after pre-treatment. The rheological measurements show reduced polyphosphate dispersion properties with reduced pH, increased temperature and at high calcium concentrations which correlate with directly measured and reported changes in the polyphosphate structure. When pH, temperature and high divalent cation concentrations are combined, the synergistic effect on reduced polyphosphate dispersion performance is particularly prominent.

1. Introduction

Dispersion is a key component in a wide range of mineral and material processing applications. In mineral processing, dispersants are commonly used to reduce or even eliminate aggregation, by control of slurry viscosity, during pumping to enable efficient transportation of high pulp solid loadings (Kapur et al., 1997). Dispersants are used to aid in suspending solids in a liquid as well as to control the properties of the resulting suspension. Dispersants usage in mining and mineral processing also includes scale control, filter aids, and flotation aids. Dispersion is of major importance during materials processing such as pigment processing, both for uniform pigment dispersion during the manufacturing process and to ensure discrete pigment particles for application of inorganic coatings.

Polyphosphate reagents are widely used in mineral and material processing industries as dispersants and rheological modifiers (Rashchi and Finch, 2000; Silvestre et al., 2009). Evidence suggests that longer chain polyphosphate, $(PHO_3)_n$, $n > 4$, have an improved dispersion ability over shorter chains due to adsorption where surface complexes are formed thereby presenting a charged portion of the un-complexed chain to the medium as a charged steric barrier (van Wazer, 1961; Feiler et al., 2000; Papo et al., 2002).

Polyphosphates have the ability to adsorb onto metal oxides and clay particle surfaces via electrostatic and/or chemisorption mechanisms. Specific adsorption of polyphosphate reagents is known to occur to metal oxides such as titania with the apparent viscosity of metal oxide systems decreasing upon adsorption of polyphosphates (van Wazer, 1961; Michelmore et al., 2000). Chemisorption dominates polyphosphate adsorption at alkaline conditions such as pH 9 whilst at acidic condition, such as pH 4, a combination of chemisorption and electrostatic interaction occurs (Taylor et al., 2001).

It has however been shown that aqueous polyphosphate solutions are not stable under certain conditions. Polyphosphates have been observed to hydrolyse at high temperature, acidic or basic pH, or in the presence of specific metal ions resulting in the formation of smaller phosphate molecules (van Wazer, 1958; Trotman-Dickenson, 1973). The degree of hydrolysis of phosphate chains has been also observed to increase rapidly as the chain length increases (Chaberek and Martell, 1959). It has been reported that in the presence of metal ions both complexation and hydrolysis of polyphosphate can occur (Chaberek and Martell, 1959).

As discussed above, amorphous polyphosphates in solution can be converted into phosphate of shorter chain length, by hydrolysis. The rate of conversion will vary according to the temperature and pH of the solution. While the lower polyphosphates retain, to a large extent, the properties of the original amorphous polyphosphate, further ionisable groups are introduced at the points where the chains break. A recent study of the effect of pH, temperature and time on the stability of ammonium polyphosphate fertiliser

---

* Corresponding author. Present address: JKMRC, The University of Queensland, 40 Isles Road, Indooroopilly, QLD 4068, Australia. Fax: +61 7 33465987.

E-mail address: s.farrokhpay@uq.edu.au (S. Farrokhpay).

[1] Present address: Flinders University, GPO Box 2100, Adelaide, SA 5001, Australia.

0892-6875/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.mineng.2012.07.001

solutions has shown that polyphosphate solutions are stable at neutral pH and room temperature (25 °C). In contrast, at acidic condition (pH 2.3) and high temperature (50 °C), almost all tripolyphosphate as well as 96% of polyphosphate was hydrolysed after 28 days (McBeath et al., 2007).

Smaller phosphate units such as orthophosphates which are formed during the hydrolysis process may be detrimental as they are likely to have reduced dispersion capacity. While many investigations of polyphosphate degradation are based on measuring the rate of orthophosphate formation and extrapolating that to a corresponding rate for the degradation of the polyphosphate species (Zinder et al., 1984), there has been no study undertaken, until now, to directly investigate the impact of polyphosphate hydrolysis on dispersion capacity. Rheological studies offer a direct means for investigating dispersant capacity and consequently to understand of the impact of polyphosphate hydrolysis.

This paper examines the influence of physical and chemical parameters, such as temperature, time, pH and cation concentration, upon polyphosphate dispersion efficiency. Boehmite and titania pigment suspension were used as model systems in this study. Boehmite was used as model of the titania pigment surface as spectroscopic surface analysis has shown that the titania pigment surface coating is in the form of boehmite (Morterra et al., 1992; Morris et al., 1999; Farrokhpay et al., 2004a, b). The polyphosphate dispersion properties have been investigated using rheological and infra-red spectroscopic studies.

2. Materials and methods

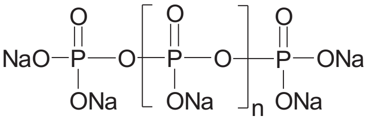
2.1. Reagents

High-purity water was produced by the following sequential treatment: reverse osmosis followed by two stages of mixed bed ion exchange, two stages of activated carbon treatment and a final filtering step through a 0.22 μm filter. The conductivity was less than 0.5 μS/cm at 20 °C.

Calgon T used was sodium polyphosphate granular obtained from Albright & Wilson (Australia) Limited. The structure of the Calgon T is presented in Fig. 1, the molecular weight ranging between 1082 and 1286 Da (ACE, 2004). Stock of 5 wt.% polyphosphate solution was prepared by dissolving 5 g of Calgon powder in 100 mL water. Stock solution was adjusted to the desired pH, calcium ion concentration or temperature, prior to addition to the suspension for rheological analysis.

The titania pigment sample used was an aluminate- and zirconia-coated, aluminium-doped rutile with a density of 4.1 g/cm^3. The BET surface area of the pigment particles measured by N_2 adsorption was 19.0 m^2/g. The mean diameter of the particles measured by Transmission Electron Microscopy (TEM) was 0.23 μm. The titania pigment isoelectric point was at pH 7.8. The major surface elements determined by X-ray photoelectron spectroscopy (XPS) were aluminium, titanium, zirconium and oxygen (19, 6, 0.6 and 74 at.%, respectively, after removing the adventious carbon contribution). The aluminate phase was the hydrated form, boehmite (AlOOH), as indicated by Auger parameters (Morris et al., 1999).

High purity boehmite, Apyral AOH 60, used throughout this study was obtained courtesy of Nabaltec, Germany with a density of 3.0 g/cm^3. The BET surface area of the boehmite particles measured by N_2 adsorption was 6.0 m^2/g. The morphology, size and shape of the boehmite particles were examined using TEM. The particles are angular and generally cubic with the average particle size of 0.75 μm, which is identical to the D_{50} value obtained in solution by laser diffraction. The major surface elements determined by XPS were aluminium, oxygen and sodium (37, 61 and 0.8 at.%, respectively, after removing the adventious carbon contribution). Surface analysis of uncoated pigment has shown the surface has boehmite surface properties character (Farrokhpay et al., 2004b), making boehmite a model system aligned to the pigment suspension. The boehmite isoelectric point was at pH 9.0.



$$\mathrm{NaO{-}\overset{\displaystyle O}{\overset{\|}{\underset{\displaystyle ONa}{\underset{|}{P}}}}{-}O{-}\left[\overset{\displaystyle O}{\overset{\|}{\underset{\displaystyle ONa}{\underset{|}{P}}}}{-}O\right]_n{-}\overset{\displaystyle O}{\overset{\|}{\underset{\displaystyle ONa}{\underset{|}{P}}}}{-}ONa}$$

Fig. 1. The chemical structure of Calgon T (n = 8–10).

All other reagents used were analytical grade (unless otherwise stated).

2.2. Rheology

Shear stress of the titania pigment or boehmite suspensions was determined at 25 °C as a function of polyphosphate concentration, using a Haake CV20 couette-type rheometer fitted with a Mooney-Ewart (45 mm diameter, 0.5 mm gap) concentric cylinder sensor. Suspensions were prepared at a solid content of 50 wt.% for pigment and 25 wt.% for boehmite, in 0.01 M KCl. After conditioning by continuous stirring overnight and then pH adjustment, the titania pigment suspensions were sheared at an increasing shear rate, from 0 to 300 s^{-1} and back to rest in 2 min with the torque sensor continuously determining the shear stress. Overnight conditioning was a critical component of the suspension preparation to ensure reproducibility and minimise rheological suspension preparation error, as observed by Nguyen et al. (2006). The yield stress (τ_B) of the suspension was obtained using the Bingham model

$$\tau = \tau_B + \eta_{pl} D \tag{1}$$

where η_{pl} is the plastic viscosity, D is the shear rate and τ is the shear stress (Hunter, 2001).

2.3. Infrared spectroscopy

A single-beam Fourier transform infrared (FTIR) spectrometer Nicolet Magna-IR System 750 fitted with a liquid nitrogen cooled mercury–cadmium–telluride (MCT) detector was used at a resolution of 4 cm^{-1} for ATR–FTIR experiments. The instrument was equipped with an ATR single reflection 45° ZnSe prism (FastIR™, Harrick, USA) in this study. Aqueous solutions were analysed by placing a drop of the sample on top of the ATR crystal.

3. Results and discussion

In order to investigate the impact of chemical and physical parameters on polyphosphate stability, freshly prepared stock solutions were conditioned at a range of pH values, temperatures, divalent metal ion concentrations and time, typically termed ‘pre-treated’ solutions. Subsequently, polyphosphate solutions were added to suspensions and rheologically analysed. Rheological characterisations of mineral slurries are important factors in determining the mineral suspension behaviour (Farrokhpay et al., 2005, 2010; Farrokhpay, 2012) and it has been used to investigate the aging of polymer systems (Laske et al., 2012).

3.1. Influence of pH and temperature on polyphosphate performance

Fig. 2 shows the yield stress of the suspension at pH 9.0 as a function of polyphosphate concentration and solution preparation conditions (freshly prepared at neutral pH or pre-treated for 24 h at pH 3.5 and 90 °C). It is clearly observed that parameters such as temperature, pH and conditioning time, can affect the dispersion