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Comparative study of dewatering characteristics of metal precipitates generated during treatment synthetic polymetallic and AMD solutions

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ABSTRACT

The sludge dewatering characteristics expressed in terms of settling, filtration and centrifugation of metal precipitates generated during treatment of polymetallic solutions and synthetic acid mine drainage have been evaluated in this research. Results show that dewatering properties of metallic sludge vary depending on the type of matrix (Cl^-; SO_4^{2-}), precipitating agent, and metals present in effluent. Metal hydroxides (at pH 10.0) and metal phosphates precipitates (at pH 7.0) are amorphous in nature, thus difficult to dewater. In these treatment methods, the substitution of chloride matrix by sulphate one improves considerably dewatering properties (specific resistance to filtration = 6.60×10^{13} and 2.35×10^{13} m/kg for the chloride and sulphate matrix, respectively). In the case of sulphide and carbonate treatments (pH 8.0), precipitates obtained are semi crystalline, and crystalline form, respectively, and no influence of the matrix was detected on dewatering characteristics.

1. Introduction

Precipitation is the most commonly used process for the removal of metals from industrial wastewaters because it offers a most cost-effective solution applicable to large operating units (Patterson, 1988; Baltpurvins et al., 1996a; Mishra, 1999; Blais et al., 2008). Many studies have demonstrated efficiency of the precipitation in removing various metals (for example, nickel, copper, zinc, cadmium and lead) as sulphide, carbonate and phosphate instead of hydroxide (McAnally et al., 1984; Preis and Gamsjager, 2001; Guillard and Lewis, 2002; Mavropoulos et al., 2002; Pigaga et al., 2002; Veeken and Rulkens, 2003; Al-Tarazi et al., 2004).

From a chemical point of view, precipitation is a complex phenomenon resulting from the formation of conditions of supersaturation. It can be described by three steps: 1) nucleation or germination; 2) crystalline growth; and 3) flocculation (Patterson, 1988). In many precipitation systems, the characteristic reaction and nucleation times are very short, of the order of milliseconds or less (Sohnel and Garside, 1992), and thus, kinetic considerations are of minor concern compared to thermodynamics.

One method that appears to be potentially useful for the prediction of effluent composition effects employs the use of solubility curves concept (Baltpurvins et al., 1996b). This involves the calculations of the treatment efficiency in terms of residual metal ion concentration vs. pH. The construction of a solubility domain is a complex process and involves the simultaneous solution of all the relevant mass action expressions for the overall system, in reference to their mass balances.

Computer simulation tools (HYDRAQL, MINEQL+, MINTEQA2, PHREEQC) incorporating extensive databases have also been developed to simulate aqueous-based chemical systems involving a variety of species over a broad range of temperature, pH and composition (Westall et al., 1976; Papelis et al., 1988; Allison et al., 1991; Parkhurst et al., 1980). These models can be used to get good approximations of the residual metal concentrations in solution for different metal precipitation scenarios (Apul et al., 2005; Halim et al., 2005).

Besides yield and selectivity, a good knowledge of settling (SVI), filterability (SRF, FC) and dewatering characteristics (TS) of the metal precipitates produced is also necessary to evaluate the techno-economic performance of different metal precipitation methods.

The purpose of this study is to illustrate the matrix effect (Cl^- vs. SO_4^{2-}) in terms of residual metal concentration and dewatering characteristics of sludge generated after hydroxide, phosphate, carbonate, and sulphide

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Nomenclature

μ	viscosity of the filtrate (Pa s)
A	surface area (m^2)
AMD	acid mine drainage
b	slope of the plot (V vs. t/V)
c	weight of solids/unit volume of filtrate (kg/m^3)
C_f	final concentration (mol/L)
C_i	initial concentration (mol/L)
D	weight of dry sludge after filtration (kg)
FC	filtration capacity ($kg/(m^2\ s)$)
I	ionic strength (mol/L)
M	bivalent metal
M_f	final moisture content (%)
M_i	initial moisture content (%)
P	pressure (Pa)
rpm	rotations per minute
S	exchanger
SRF	specific resistance to filtration (m/kg)
SVI	sludge volume index (mL/g)
t	time (s)
T_f	final time of the filtration (s)
TS	total solids (w/w)
V	volume (m^3)
XRD	X-ray diffraction

precipitation of polymetallic solutions. These parameters are also studied in the case of sludge generated from two typical compositions of synthetic AMD. All residual metal concentrations have been compared to those calculated with MINEQL+ software.

2. Materials and methods

2.1. Solubility domain predictions

Solubility domains were calculated using the chemical equilibrium modelling system MINEQL+ (version 4.5). This program may be used to compute equilibrium among dissolved, solid and adsorbed phases suitable for aqueous solutions based on the appropriate thermodynamic stability constants. In the present study, models were constrained to include only those solid phases that were found to govern solubility (example: oxides are not considered due to kinetic considerations). Ionic strength was considered “off” within the program. All calculations were performed at a constant temperature of 298 K with the number of iteration cycles constrained to 100. Solubility domains were generated for four systems: hydroxides and phosphates for the first polymetallic solution (Fe^{3+}, Al^{3+}, Zn^{2+}, Cu^{2+} and Ni^{2+}), and sulphides and carbonates for the second polymetallic solution (Fe^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+} and Cd^{2+}). The counter ion is sulphate (SO_4^{2-}) for all systems. The concentration of all metals was always initially set at 4.00×10^{-3} mol/L. Calculations were made over the pH range 2–14, for hydroxide and phosphate, and 5–14 for sulphide and carbonate systems.

2.2. Adsorption prediction

Adsorption prediction of Ni and Zn ions onto ferrihydrite in the case of neutralized AMD1 was modeled using the Two-Layer FeOH adsorption model from MINEQL+ (version 4.5). A surface complexation database for sorption of inorganic species on $Fe(OH)_3$ (s) is included in the MINEQL+ thermodynamic database. These surface complexation reactions and constants were taken from Dzombak and Morel (1990) and were readily incorporated in geochemical speciation codes, and have been gainfully employed in understanding metal speciation in such diverse aquatic environments as acid mine drainage (Ball et al., 2001).

The system is defined as follows: total ferric iron of 1.29×10^{-2} mol/L; total zinc of 4.59×10^{-6} mol/L; total nickel of 1.02×10^{-6} mol/L; ionic strength I of 0.46 mol/L; and pH of 10.0.

2.3. Preparation of the polymetallic solutions

Polymetallic synthetic solutions having a concentration $[M^{n+}]$ of 0.004 mol/L for each metal were prepared starting from metal sulphate or chloride salts: Fe^{2+}, Fe^{3+}, Zn^{2+}, Mn^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} (Lab Mat), Al^{3+} (Baker). Distilled water was used for all the experiments. In the case of hydroxide precipitation assays, the pH of polymetallic solutions was firstly adjusted to 2.0 with HCl 6.0 mol/L or H_2SO_4 3.0 mol/L (Fisher Scientific Ltd., ACS reagent) for the chloride and sulphate matrix, respectively.

Four polymetallic solutions were prepared:

- *Sln A*: contains Fe^{3+}, Al^{3+}, Zn^{2+}, Cu^{2+} and Ni^{2+} in chloride matrix;
- *Sln B*: contains Fe^{3+}, Al^{3+}, Zn^{2+}, Cu^{2+} and Ni^{2+} in sulphate matrix;
- *Sln C*: contains Fe^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+} and Cd^{2+} in chloride matrix;
- *Sln D*: contains Fe^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+} and Cd^{2+} in sulphate matrix.

2.4 Preparation of the AMD solutions

Two typical compositions of acid mine drainage (AMD1 and AMD2) were studied in this work. Composition of the AMD1 was selected on the basis of the median concentrations of 10 AMDs of mining sites reported in the literature (MEND, 1994). AMD2 composition was also determined using median from metal concentration values of 11 AMDs reported in Gilbert et al. (2003), Demopoulos et al. (1995), Hammarstrom et al. (2003), Yabe and Oliveira (2001), Feng et al. (2004), Wurzburger and Overton (2004), Tabak et al. (2003), Cocos et al. (2002), Chartrand and Bunce (2003) and MEND (1996).

AMD solutions were prepared starting from metal sulphate salts to 1.5 L of distilled water. In addition H_2SO_4 3.0 mol/L and Na_2SO_4 (Fisher Scientific Ltd., ACS reagent) were added to achieve pH = 2.73, $[SO_4^{2-}] = 8.43\times10^{-2}$ mol/L for AMD1 and pH = 2.48, $[SO_4^{2-}] = 5.38\times10^{-2}$ mol/L for AMD2.

2.5. Precipitation assays

Precipitation tests were realized at ambient temperature (22 ± 2 °C) and with volumes of 1.5 L of each solution in 2.0 L beakers (diameter 125 mm). Mixing of solution was conducted using magnetic stir bar (length: 37 mm, diameter: 8 mm) with a speed mixing of 160 rpm. Speed mixing was determined with a Digital Photo Tachometer Model 461893 Extech instruments. For each working pH, a reaction time of 20 min was allowed for the system to reach equilibrium (Hove et al., 2008).

Precipitation tests were realized with the following five precipitating agents: 1) sodium hydroxide (2.5 mol NaOH/L); 2) lime (20 g $Ca(OH)_2$/L); 3) sodium sulphide (Na_2 S); 4) disodium hydrogen phosphate (Na_2HPO_4); and 5) sodium bicarbonate ($NaHCO_3$).

Hydroxide precipitation tests were done by adjusting pH solutions (volume of 1.5 L) to 10.0 with the sodium hydroxide or lime solution. Precipitating agents were added in stoichiometric proportion (with a slight excess) with the soluble metal concentrations present in solution.

During the other precipitation tests, precipitating agents were firstly added to solutions. A pH adjustment was done by adding sodium hydroxide to 7.0 for phosphate and 8.0 for carbonate and sulphide systems. To note that in the case of sulphides and carbonates, an initial adjustment of the pH in values close to 5.50 was made to