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# Carboxymethylcellulose (CMC) as PbS depressant in the processing of Pb-Cu bulk concentrates. Adsorption and floatability studies

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## ABSTRACT

Adsorption of CMC on galena (PbS) was investigated through electrokinetic, adsorption and ATR-FTIR spectroscopic studies. In addition, CMC adsorption on chalcopyrite ($CuFeS_2$) was carried out to compare it to that on PbS. The effect of CMC on the floatability of PbS and $CuFeS_2$ was assessed by microflotation using PbS and $CuFeS_2$ crystals and ethyl xanthate as collector. Furthermore, the effect of oxidation of the minerals on the floatability and CMC adsorption was studied. CMC adsorption on PbS took place within a pH range of significant concentration of the hydroxo-complex species $PbOH^+$ wherein the COOH group of the CMC is as $COO^-$. It is proposed that CMC adsorbs through intramolecular electrostatic and acid/base interactions between the $COO^-$ and $PbOH^+$ at the PbS/aqueous solution interface. Adsorption of ethyl xanthate on PbS is more stable than that of CMC. Oxidation creates $SO_4$ species on the PbS surface promoting co-adsorption of CMC, through which the PbS surface becomes hydrophilic on top of the hydrophobicity due to adsorbed ethyl xanthate. Upon oxidation, the high PbS floatability was largely hindered by CMC while that of $CuFeS_2$ was not affected. Flotation strategies are presented for the application of the non-toxic polysaccharide CMC as a depressant of PbS in the separation of Pb-Cu bulk concentrates while floating $CuFeS_2$.

## 1. Introduction

Dextrin and starch are extensively used in the processing of Pb-Cu bulk concentrates to selectively depress galena (PbS) allowing the flotation of chalcopyrite ($CuFeS_2$). This scheme is employed for bulk concentrates with a Pb/Cu mass ratio larger than one and the copper is as chalcopyrite ($CuFeS_2$) in the concentrate. Such scheme can also be applied for bulk concentrates with a Pb/Cu mass ratio lower than one and the copper is as secondary copper minerals such as covellite (CuS), chalcocite ($Cu_2S$), digenite ($Cu_9S_5$) and bornite ($Cu_5FeS_4$). This is because of the high solubility of these copper minerals with the cyanide compounds which are used to inhibit the flotation of copper (Wills, 1984; López-Valdivieso, 2007).

Prior to the addition of dextrin and starch, the Pb-Cu bulk concentrate is treated with sulfur dioxide ($SO_2$). Sulfoxy salts such as sodium sulfite ($Na_2SO_3$), sodium bisulfite ($NaHSO_3$), ammonium bisulfite ($NH_4HSO_3$) and sodium metabisulfite ($Na_2S_2O_5$) can be used instead of $SO_2$. The depression of galena with temperature has been practiced at various plants (Kubota et al., 1975; Twidle and Engelbrecht, 1984; McTavish, 1980). This galena depression can also be achieved with chromate salts (Wills, 1984; Bolin and Laskowski, 1991). Chromates with Cr(VI) are highly carcinogenic to humans and toxic to the environment so that their use should be avoided or the plant water should be treated for Cr(VI) removal. The non-toxic ferric chloride ($FeCl_3$) and sodium thiosulfate ($Na_2S_2O_3$) have also been recommended for galena depression (Aseeva, 1978).

Carboxymethylcellulose (CMC) is an environmentally friendly chemical reagent as are dextrin and starch. Bultatovic et al. (2001) reported the plant use of CMC in a mixture with sodium dichromate ($Na_2Cr_2O_7$) and disodium phosphate ($Na_2HPO_4$) to depress lead in copper flotation of a bulk concentrate containing PbS, $CuFeS_2$ and secondary copper minerals. Other than that not much is known about the CMC industrial application in Pb-Cu separation. In addition, the underlying adsorption mechanisms of CMC on PbS is unknown. CMC may be more effective and selective than dextrin and starch for PbS depression because of the carboxyl group (COOH) in the CMC molecular structure. CMC is industrially employed as a regulator to hinder the natural floatability of talc in PGE flotation (Bulatovic, 1999; Corin and Harris, 2010) and as a blinder of water-insoluble minerals in KCl flotation (Pawlik et al., 2003).

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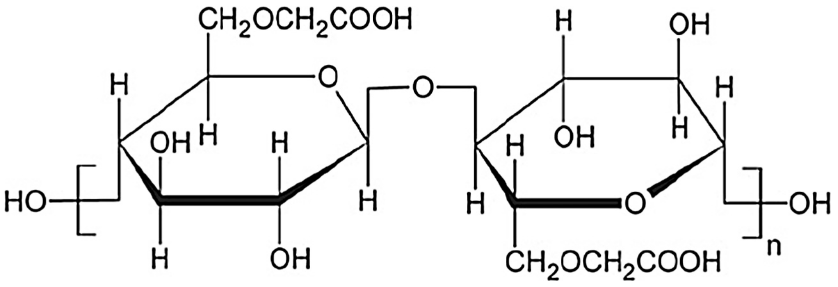

**Fig. 1.** Molecular structure of CMC.

The aim of this work was to shed light on the adsorption mechanism of CMC on PbS. The surface conditions that the PbS has in a Pb-Cu bulk concentrates was taken into account to establish flotation chemical routes for the use of CMC as a Pb depressant in the processing of these concentrates. Chemical species on PbS was characterized by FTIR spectroscopy and electrokinetics. CMC adsorption studies were also carried out on $CuFeS_2$ to gain insights on the adsorption difference between PbS and $CuFeS_2$. The effect of CMC on the floatability of these minerals was studied through microflotation using ethyl xanthate as the collector.

## 2. Experimental

PbS crystals from Chihuahua, México and $CuFeS_2$ crystals from Durango, México were used in this work. Microflotation tests were performed with −75 + 45 μm size particles and −45 μm size particles were prepared for electrokinetics, adsorption and spectroscopy. The specific surface area of the −45 m size particles was determined by the BET technique and found to be 0.19 $m^2/g$ and 0.40 $m^2/g$ for PbS and $CuFeS_2$, respectively. CMC from Polyscience Inc with 99.9% purity and molecular weight of 80,000 g/mol was used in this work. The DS of this CMC is 0.7, which means that there are 7 substitutions in 10 glucose units of the 30 possible substitutions. Pure potassium ethyl xanthate was used as collector. This pure xanthate was prepared from a technical grade xanthate supplied by Industrias Químicas de México. The purification procedure involved dissolving the xanthate in acetone, followed by its recrystallization in ethylic ether. This procedure was done threefold to ensure that the recrystallized xanthate was of high purity. All aqueous solutions were prepared with de-ionized water. The pH of PbS suspensions was adjusted with dilute HCl or NaOH solution. NaCl was used as electrolyte to fix the ionic strength of the aqueous solutions at 0.01 mol/L.

Microflotation tests were carried out using a modified Hallimond tube, one gram mineral and 100 mL aqueous solution at the desired concentration of xanthate, hydrogen peroxide ($H_2O_2$) and CMC. Prior to flotation, the minerals were contacted with each of the chemicals for 30 min. The pH of the suspensions was 5 and was kept constant during conditioning. Flotation time was one min using nitrogen at a flow rate of 30 mL/min. CMC adsorption was carried out using one gram mineral and 100 mL aqueous solution at the desired $H_2O_2$ and CMC concentration. The minerals were contacted with the $H_2O_2$ and CMC for 30 min at the desired pH. Afterwards, the suspension was allowed to stand for a few minutes for solid settling, then the supernatant was collected and centrifuged for 15 min at 3900 rpm using a Sigma model 2–5 centrifuge. Residual CMC concentration was determined following the procedure reported by Dubois et al. (1956). Chemical species were characterized by FTIR spectroscopy using the ATR technique. This spectroscopic studies were carried out in a Thermo Scientific Nicolet iS10 with 0.4 $cm^{-1}$ spectral resolution. The mineral particles in contact with the solution were deposited on a diamond crystal, the ATR element. The mineral particles were pressed against the ATR element to assure contact between them. A He/Ne laser was used as the infrared beam.

The electrophoretic mobility of PbS was determined using a Riddick ZM-75 Zeta Meter. 0.3 g PbS and 100 aqueous solutions were used and the PbS was conditioned with the $H_2O_2$ and CMC for 30 min. The pH was adjusted to the desired value. The electrophoretic mobility was transformed to zeta potential through the Smoluchowski equation.

## 3. Results and discussion

### 3.1. CMC hydrolysis

CMC comes from natural cellulose treated with chloroacetic acid ($ClCH_2CO_2H$). In CMC, a carboxymethyl group ($-CH_2-COOH$) is linked to some of the hydroxyl groups of the glucose unit connected by −C−O−C ether bonds in the cellulose backbone. The CMC molecular structure is shown in Fig. 1.

The CMC carboxyl group COOH ionizes with pH giving rise to the anionic group $COO^-$ as follows:

$$-CH_2 - COOH = CH_2 - COO^- + H^+ \qquad K_i = [H^+][-CH_2 - COO^-] \qquad (1)$$

The Ki of the CMC used in this work was found to be 3.8, which was determined through conductivity measurements of CMC aqueous solutions. With this Ki value, a species distribution diagram was built for the non-ionized and ionized groups of CMC. This diagram is presented in Fig. 2 showing that the non-ionized COOH is predominant below pH 2 and the anionic $COO^-$ above pH 6. Equal proportion of these two

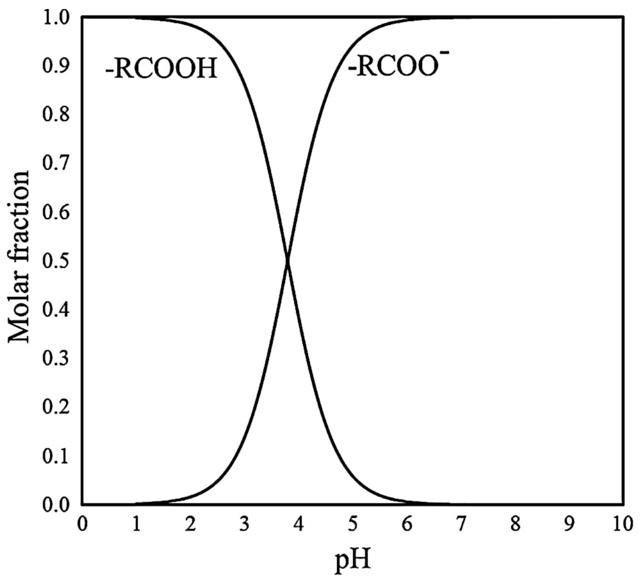

**Fig. 2.** Speciation diagram of carboxyl groups in CMC as a function of pH.