

Study of the adsorption of collectors and depressants onto calcite by high frequency dielectric measurements



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ABSTRACT

It is possible to analyze in situ the adsorbate/adsorbant interaction during the flotation process by high frequency dielectric measurements. The adsorption of complexing collector (sodium oleate) onto calcite increases the dielectric permittivity independently of the frequency. The dielectric constant increases after adsorption because the adsorbate and the adsorbant interact through covalent bonds. Physical adsorption involving electrostatic interactions or hydrogen bonds (dodecylamine and dodecylsulfate) has no effect on the dielectrical characteristics. The dielectric method allows to analyze the mechanisms of depression using reagents such as quebracho and sodium silicate.

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1. Introduction

The separation of calcite from precious minerals such as smithsonite, fluorite, scheelite, apatite and celestite by selective flotation is extremely complex and requires an accurate analysis of the phenomena at the liquid/solid interfaces (Antti and Forssberg, 1989; Hiçiyılmaz et al., 1993; Irannajad et al., 2009; Martínez et al., 2003; Shi et al., 2013 and Song et al., 2006). This detailed analysis of the reaction processes has made notable progress with the development of methods such as photoelectron spectrometry (XPS), atomic force microscopy (AFM), Fourier transform infrared spectrometry (FTIR) and zeta potential measurements (Quast, 2016; Bo et al., 2015; Yang et al., 2015; Shi et al., 2013; Fa et al., 2006; Rezaei Gomari et al., 2006; Sayan, 2005 and Gurpinar et al., 2004). It is thus possible to characterize the surface of the divided solid despite the low concentration of the collectors or depressants used. It should be noted, however, that these techniques require a processing of the mineral sample and heavy expensive equipment.

Fundamentally, the adsorption of collectors and depressants on the mineral surface of calcite results from a number of forces linked to the existence of interaction of electrostatic type, covalent type or hydrogen bonding. In the case of an electrostatic interaction, the surfactants are adsorbed on the mineral surface by a bond between the polar head of the collector ion and the charged electrical double layer on the mineral

surface (Yang et al., 2015; Hosseini and Forssberg, 2006; Martínez et al., 2003; López-Valdivieso et al., 2000; Hiçiyılmaz et al., 1993; Leja, 1982; Smani et al., 1975 and Cases, 1970). When the collector has the property of complexing the calcium of the mineral surface, it establishes an energetic bond between the adsorbate and the adsorbent, provided that the interface is stable. In this case, the studies have shown that a chemisorption phenomenon is involved (Quast, 2016; Gao et al., 2016; El-Mofty and El-Midany, 2015; Cebeci and Sonmez, 2004; Sonmez and Cebeci, 2003; Young and Miller, 2000; Sivamohan et al., 1990 and Rao et al., 1991).

The development of high-frequency dielectric techniques has led to interesting results in the process of activation of the sphalerite by the Cu^{2+} ions, the malachite by the S^{2-} ions and the zeolites microparticles by the S^{2-} ions (Bessièrè et al., 1986, 1990, 1991 and Walcarius et al., 2006). The method can also identify the nature of the adsorbate/adsorbent bond during the adsorption of the collectors on the surfaces of the conductive minerals and salt-type compounds (Bessièrè and Khayar, 1993; Bessièrè and Etahiri, 1994; Bessièrè et al., 1995a and Etahiri et al., 1997 and Khayar and Bessièrè, 2008). This technique has been also proposed for the control of the behaviour of ion-exchange resins (Bessièrè et al., 1995b; Machal-Heussler et al., 2000), for the characterization of activated carbon (Akhouaou et al., 2000) and for monitoring the apatitic cement setting reaction (Despas et al., 2014).

The present work analyzes the capability of dielectrical method to distinguish a chemisorption of a physisorption during the flotation of the calcite with collectors such as oleate, dodecylsulfate and

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dodecylamine. We also study the sensitivity of the technique to analyze the mechanisms of depression using reagents such as quebracho and sodium silicate.

2. Method and experimental procedure

2.1. Dielectric method

The dielectric method consists in measuring the complex impedance Z^* of the decanted mineral pulp in a capacitive cell (Fig. 1) to which a high frequency electric field was applied [0.4–150 MHz] (Bessière et al., 1986, 1990, 1991 and Despas et al., 2014).

For a non-conductive pulp, Z^* values can be transformed in the complex permittivity $\varepsilon^* = \varepsilon' - j\varepsilon''$ where ε' is the dielectric constant and ε'' the permittivity of pulp according to following equation (Bussey, 1980):

$$Y^* = \frac{1}{Z^*} = Y_0 \sqrt{\varepsilon^*} \operatorname{th} \sqrt{-\varepsilon^* \omega l / c}$$

Y^* : Admittance of the cell filled with the decanted pulp,
 Y_0 : Characteristic admittance of the empty cell,
 l : Electrical length of the cell,
 c : Velocity of light.

If the measurement frequency is sufficiently low or if the effective length of the cell is small, the “th” function can be replaced by its limited development. So, the admittance of the cell can be calculated by the approximate formula (Gottmann and Dittrich, 1984):

$$Y^* = \frac{1}{R} + jC_a \omega = C_a \varepsilon'' \omega (1 + \beta \varepsilon' \omega^2) + jC_a \varepsilon' \omega (1 + \alpha \varepsilon' \omega^2)$$

C_a , α , and β are the cell parameters. They are easily obtained by calibrating the cell with a known permittivity liquid (distilled water, ethanol).

2.2. Experimental procedure

Pure calcite is ground in an agate mortar in the presence of water (particle size range: $40 < d < 80 \mu\text{m}$). Sodium oleate, dodecylsulfate, dodecylamine and sodium silicate are of analytical grade. The quebracho was provided by Mineralia Silius.

The flotation tests were carried out in a hallimond tube. The density of the pulp was 4% and the volume of the solution was 100 ml (4 g/100 ml). The pulp was continuously stirred, for 2 min with a pH

regulator, 5 min with the depressant and 5 min with the collector. The duration of flotation was 2 min (air flow rate: 10 l/h). The pH values were set at the natural pH (9.8) for sodium oleate, pH = 5 for dodecylsulfate and pH = 11 for dodecylamine.

The impedance measurements were carried out at 21 °C on the pulp (4 g of solid) after decantation in the capacitive cell. The values of Z^* were recorded by an HP 4194A impedance/gain-phase analyser (Hewlett–Packard). The experimental device was connected to a computer allowing real-time calculation of the dielectric permittivity ε' and dielectric losses ε'' . All measurements were repeated three times and led to similar results, giving evidence of the good reproducibility of this technique.

3. Results and discussion

3.1. Dielectrical behaviour of pure calcite

Frequency and ionic strength are fundamental parameters which determine the dielectric characteristics of the calcite pulp. Their influences depend on the optimum conditions for detecting the adsorption of collectors and depressants on the surface of the mineral.

3.1.1. Frequency

In the frequency range examined [0.4–150 MHz], the dielectric constant ε' is independent of the frequency. The dielectric permeability ε'' decreases as the frequency increases (Table 1). Therefore, a single measurement with fixed frequency is sufficient to characterize the mineral pulp by its value ε' .

3.1.2. Ionic strength

It is important to know if the presence of ionic species in solution represents an obstacle to the dielectric characterization of the mineral pulp. This leads us to examine the effect of ionic strength on the dielectric response of the mineral/solution system.

To quantify this effect, the calcite pulps were equilibrated with sodium nitrate at different concentrations. We suppose that there is no interaction between salt ions and the surface of the mineral.

The results (Table 1) clearly show that the dielectric constant of the system is substantially independent of the ionic strength for salt concentrations of $< 10^{-1}$ M. These concentrations are much larger than those of the collector (5.10^{-5} to 10^{-4} M). On the contrary, the values of ε'' increase with the concentration of electrolyte. It can be concluded that the presence of ions in high concentration does not interfere with the dielectric characterization of the properties of the solid/solution interface.

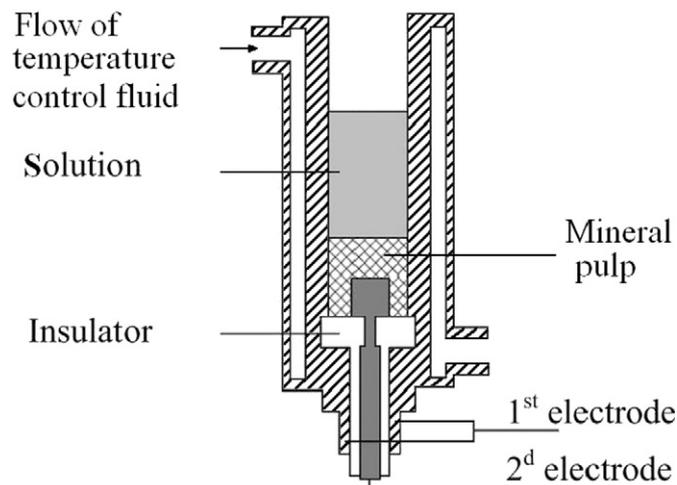


Fig. 1. Dielectric cell.

Table 1

Frequency and ionic strength effect on dielectrical characteristics of pure calcite. (T = 21 °C).

Calcite + solution	Frequency (MHz)	ε'	ε''
H ₂ O	5	37.3	9.5
	10	37.6	6.5
	50	37.0	5.7
NaNO ₃ 10 ⁻⁵ M	5	38.0	13.6
	10	37.7	6.9
	50	38.1	1.6
NaNO ₃ 10 ⁻⁴ M	5	38.7	14.4
	10	38.3	7.2
	50	38.7	1.7
NaNO ₃ 10 ⁻³ M	5	38.6	37.3
	10	38.2	13.8
	50	38.1	3.0
NaNO ₃ 10 ⁻² M	5	41.4	154
	10	39.9	77.6
	50	39.4	15.2
NaNO ₃ 10 ⁻¹ M	5	72.5	1170
	10	52.1	592
	50	40.7	123

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