



Flotation in concentrated electrolyte solutions[☆]



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ARTICLE INFO

Article history:

Received 8 April 2015

Received in revised form 6 September 2015

Accepted 28 September 2015

Keywords:

Salt flotation

Seawater

Seawater flotation

Cu–Mo ores flotation

Fatty acids

Long-chain amines

Potash ore flotation

ABSTRACT

In the flotation in highly concentrated electrolyte solutions not only ionic strength but also chemical composition, flotation pH and mineral properties play an important role. As a result an improvement or depression may be observed. A strong improvement in the floatability of hydrophobic bituminous coals and other inherently hydrophobic minerals is characteristic for the “salt flotation process”, which is carried out in concentrated electrolyte solutions at natural pH and without addition of any flotation reagents. However, pH is a key factor when saline waters with hydrolyzing metallic ions are used as a process water. In the case of flotation of Cu–Mo sulfide ores in seawater, molybdenite is strongly depressed by the Mg^{2+} hydrolysis products when pH is raised to depress pyrite. The process waters with a high content of Mg^{2+} and Ca^{2+} ions, and this also includes seawater, have deleterious effect on the anionic flotation of industrial minerals with fatty acids due to the precipitation of Ca/Mg fatty acid salts. The flotation of potash ores is carried out in NaCl–KCl saturated brine (6–7 mol/L of NaCl and KCl) with the use of long-chain primary amines. Such a high electrolyte concentration changes dramatically the amine Krafft point making the collector insoluble in brine; its mode of action entirely differs from that in conventional flotation processes.

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1. Introduction

Mineral processing unit operations are commonly grouped into four distinct clusters: comminution–classification, separation, product dewatering and water clarification. In the closed circuits of modern mineral processing plants water after use is recirculated and thus

becomes a concentrated electrolyte solution. Its concentration may be as high as 1 M NaCl (e.g. Mt. Keith plant in Australia); flotation of potash ores is carried out in NaCl–KCl saturated brine that is at these salts concentration exceeding 6 mol/L (e.g. plants in Saskatchewan in Canada). The use of seawater in flotation has been extensively studied and it is already used in several plants (e.g. Las Luces concentrator at Taltal in Chile, Esperanza concentrator at Sierra Gorda in Chile).

Distinct unit operations require the use of different chemical additives. For instance, while dispersing agents may be needed in grinding, collectors and modifying agents are utilized in flotation, solid–liquid separation processes (thickening and filtration) commonly require the

[☆] This paper is based on the paper presented at the 27th International Mineral Processing Congress, Santiago, October 20–24, 2014.

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use of flocculants. These are high molecular weight polymers and it cannot be expected that the chemical compounds so different from collectors will respond similarly to an increased ionic strength of the pulp.

The topics considered in this paper are limited to the flotation and flotation reagents. Polymeric compounds referred to as flocculants are typical lyophilic colloids and they are quite different from flotation reagents. Quite different is also the effect of electrolyte concentration on their properties from the effect of electrolyte concentration on flotation collectors. The effect of ionic strength on flocculation is dealt with in a different paper (Huang et al., 2013).

For the sake of discussion, in the present work the systems in which flotation is carried out in concentrated electrolyte solutions will be classified into the following groups:

1. High ionic strength systems;
 - (a) Without pH adjustment; example: “salt flotation” of inherently hydrophobic solids, e.g. flotation of a bituminous coal in NaCl solution.
 - (b) With pH adjustment; example: flotation of Cu–Mo sulfide ores in seawater when pH is raised to depress pyrite.
2. The systems in which collector precipitates with ions present in the pulp; example: anionic flotation of phosphate ores with fatty acids in hard/seawater.
3. Flotation in saturated brine; example: separation of sylvite (KCl) from halite (NaCl) in potash ore flotation.

2. High ionic strength systems

2.1. Salt flotation (high ionic strength systems without pH adjustment)

Flotation of inherently hydrophobic minerals in concentrated solutions of electrolytes does not require the use of any other reagents. In Klassen's publications this is referred to as “salt flotation” (Klassen and Mokrousov, 1963).

For the flotation to be successful the bubbles:

- (i) must be fine enough (the flotation rate constant is proportional to the bubble surface area flux which increases with decreasing bubble size);
- (ii) and the attachment of the mineral particles when they collide with bubbles must be possible within the milliseconds of the particle–bubble contact time.

In flotation process the size of bubbles is determined by bubble coalescence that can be prevented by a frother. Frothers are best characterized by their critical coalescence concentration (Cho and Laskowski,

2002a, 2002b). As Fig. 1a shows, the critical coalescence concentration of MIBC in water is about 10 ppm. At the concentrations higher than that the bubbles generated in MIBC solutions are stable and do not coalesce. However, bubble coalescence can also be prevented by increasing electrolyte concentration. In concentrated electrolyte systems, as shown in Fig. 1a, the bubbles are stable and do not coalesce even in the absence of a frother (Laskowski et al., 2003).

This is further illustrated in Fig. 1b. As this figure shows, in distilled water fine bubbles can be generated only in the presence of a frother. However, the same process when carried out in seawater leads to the formation of fine bubbles even without any frother (Castro et al., 2010; Castro et al., 2013). These results then prove that fine bubbles can be generated in a flotation machine without the use of a frother in concentrated electrolyte solutions.

In the flotation process, mineral particles that are to be floated, are made hydrophobic by adsorbing collector. Inorganic ions cannot make solid surfaces hydrophobic. The salt flotation then must depend on initial solid hydrophobicity. Klassen in his Coal Flotation monograph (Klassen, 1962) used Kharlamov's data to demonstrate that only bituminous coals, the coals which are very hydrophobic, float well in 0.5 M NaCl solutions. 20 years later this was clearly confirmed (Fig. 2). In these tests carried out at Berkeley University (Fuerstenau et al., 1983) various coals from different mines were used in the batch flotation experiments and the wettability of these coal samples were characterized by measuring the equilibrium moisture content. As it is known, while the equilibrium moisture content in bituminous coals is very low (can be lower than 1%), it is much higher for more hydrophilic low rank subbituminous coals and lignites. This was experimentally confirmed by Fuerstenau et al. (1983) as shown in Fig. 2. Salt flotation tests carried out in 0.5 M solution of NaCl with coals varying in rank clearly demonstrate that the less hydrophobic sub-bituminous coals (which are characterized by a high moisture content) poorly float under such conditions while the salt flotation of hydrophobic bituminous coals (which are characterized by a very low equilibrium moisture content) is very satisfactory.

As shown by Laskowski and Kitchener (1969), very hydrophobic surfaces (methylated silica) can carry a substantial negative charge. Existing experimental evidence (Beattie, 2007) is consistent with the idea that water at the low dielectric surfaces (air, oil, solid hydrocarbons) acquires a negative charge above pH 3–4 from the preferential adsorption of hydroxide ions. Because of this charge, the metastable wetting film is formed on such hydrophobic surfaces (Blake and Kitchener, 1972) and as a result when such particles collide with bubbles the energy barrier opposes the attachment. This is consistent with the concept of induction time. Since electrical double layer is compressed when electrolyte concentration increases, in the case of

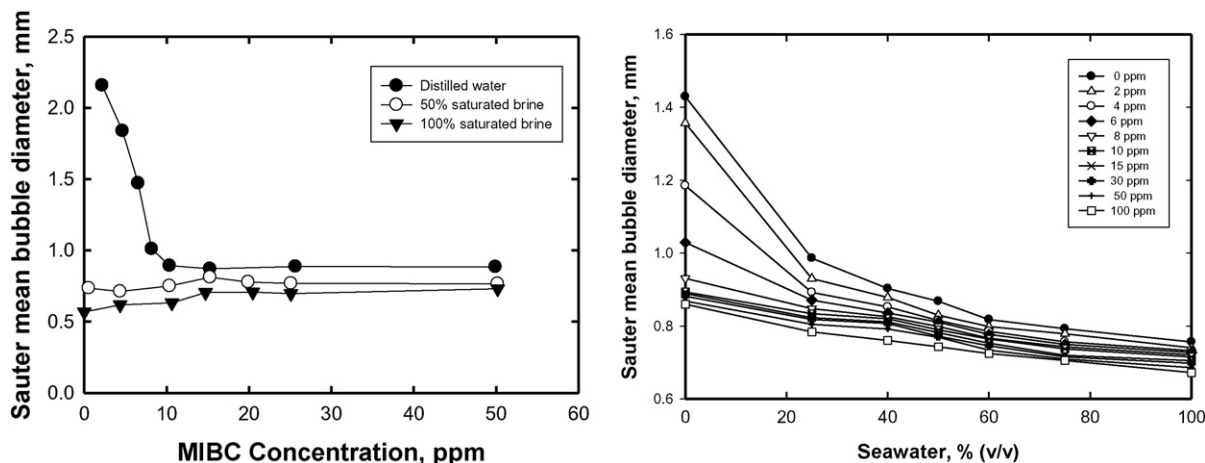


Fig. 1. a. Sauter mean bubble diameter as a function of MIBC concentration and electrolyte concentration (Laskowski et al., 2003). The term “brine” used here stands for saturated solution of KCl + NaCl (about 6 mol/L). b. Effect of the frother MIBC on bubble size in sea water (Castro et al., 2010).

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