Physicochemical Problems of Mineral Processing

Metahydrophobicity and orthohydrophilicity tested in flotation of NaCl, KCl, KPF$_6$ in their saturated aqueous solutions

Jan Drzymala, Malgorzata Dubiel, Tomasz Ratajczak

Wroclaw University of Science and Technology, Faculty of Geoengineering, Mining and Geology, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland

Corresponding author: jan.drzymala@pwr.edu.pl (Jan Drzymala)

Abstract: Flotation tests of different size fractions of NaCl, KCl and KPF$_6$ in their saturated aqueous solutions were performed in a 36 cm in height monobubble Hallimond tube. Also contact angle tests by means of sessile drops of saturated salt solution put on pressed discs of salts were carried out. The obtained sessile drop contact angles were equal to zero, pointing to a complete hydrophilicity (orthophilicity) of the investigated salts. In the case of NaCl and KCl, their orthohydrophilicity was confirmed by flotation tests and flotometric considerations because the entrainment factors, which take into account the maximum size of entrained particles and density of the salt as well as it solution, were similar to those of quartz and magnetite and equal to 0.11 mm. The entrainment factor for KPF$_6$ was equal to 0.18 mm and was greater than that of NaCl and KCl indicating certain natural flotation of this salt caused by some flotational hydrophobicity called in this paper metahydrophobicity. The metahydrophobicity of KPF$_6$ was confirmed by flotation results. In the case of KPF$_6$ the maximum yields of the same size particles were the highest, even though the density of this salt was greater than that of NaCl and KCl. Also, the first order kinetic constants were always the greatest for KPF$_6$. Further flotometeric calculation based on the balance of forces involved in flotation indicated that the estimated contact angle of KPF$_6$ was about 8° assuming static flotation, and 7° for dynamic flotation, while for NaCl and KCl was below 5°. It means that during flotation test orthohydrophilic NaCl and KCl are only entrained while for metahydrophobic KPF$_6$ there is mostly entrainment and some flotation.

Keywords: flotation, contact angle, hydrophobicity, hydrophilicity

1. Introduction

The interfacial properties of salts in their aqueous solutions are important for understanding and practical application of many phenomena, including flotation. For instance, Miller et al. (1992) investigated electrical charge of soluble salts in saturated solution and its importance in salts flotation in the presence of amines. Another essential salts property is possible natural floatability in saturated aqueous solution, resulting from the non-zero angle formed in the salt/air/salt saturated aqueous solution system. The list of naturally floating salts (in Hallimond tube, as they do not float without frother in conventional flotation machines) includes AgI, CaF$_2$ and many sulphides (Drzymala, 2007). However, there are salts which contact angle has not yet been measured. One of them is KPF$_6$. This salt is unique because its surface tension decreases with concentration in water (Lyklema, 1993) and the flotation yield of naturally floating materials, for instance coal, in the presence of KPF$_6$ slightly decreases with increasing the KPF$_6$ concentration (Lipniarski et al., 2015). It can be speculated that the main reasons for the flotation yield decrease with increasing the KPF$_6$ concentration is decreasing surface tension of aqueous solutions (Ratajczak and Drzymala, 2003). Another factor can be low concentration of saturated KPF$_6$ aqueous solutions which facilitates increasing charging of interfaces and flotation

drop (Li and Somasundaran, 1993). This property of KPF_6 is in contrast to many other salts, including KCl and NaCl, which presence improves flotation.

The aim of this research was to determine the contact angle and check possible natural floatability of KPF_6 in its own saturated aqueous solutions. The contact angle was measured by the sessile drop (Adamson, 1982) and flotometry (Drzymala, 1994a) methods. The flotometry method is based on measuring flotation yields of different size fractions of a material and calculation of the contact angle using an equation based on balance of forces involved in flotation. Both static and dynamic approaches to flotometric contact angle calculations are available (Kowalczuk et al., 2011). The measurements were also conducted for NaCl and KCl for comparison purpose.

2. Terms of hydrophobicity

There is a problem with terms hydrophobicity and hydrophilicity, because their meaning in colloid and surface chemistry is different from that in the flotation science and technology. In flotation, as well as in colloid and surface chemistry, materials are called hydrophobic when their contact angle with the aqueous phase, in the presence of air as the gas phase, is above 90º (Drelich et al., 2011). The contradiction appears in the range of 0-90° because that range indicates hydrophilicity in colloid and surface science, while in flotation it means hydrophobicity. There is an agreement in both fields that for hydrophilic materials the contact angle is equal to zero. A trial of reconciliation was undertaken by Drelich et al. (2011). They proposed to use the terms weakly hydrophilic and weakly hydrophobic for contact angles between 0-56° and 56-0º, respectively. In their classification they also included superphydrophobicity and superhydrophilicity, which are characteristic for rough surfaces. These terms consist of words hydrophobicity and hydrophilicity and a prefix *super* for a more detailed specification. It seems to be very informative and practical to use *super* and such prefixes as *ortho* (correct/straight), *meta* (following/after) and *para* (similar), which are already used in chemistry, rather than descriptive words such as either weakly or strongly. The proposed here classification of types of hydrophobicity and hydrophilicity and their relations with the contact angle is presented in a graphical form in Fig. 1.
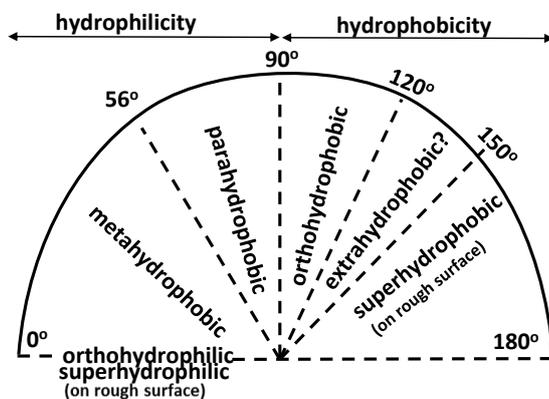
Fig. 1. Graphical representation of hydrophobicity and hydrophilicity based on contact angle and proposed names of sub-regions designed to unify the terms used in colloid and surface science as well as in flotation

Thus, the general terms hydrophilicity and hydrophobicity can be applied, as usually, for surfaces with the contact angle between 0 and 90, and between 90º and 180°, respectively. These ranges can be further divided in subranges. According to the proposed classification, materials having the contact angle equal to zero, as being fully hydrophilic, are orthohydrophilic. The hydrophilic material with the contact angle within 0-90° can be called metahydrophobic when their contact angle is between 0º and 56º while between 56° and 90° parahydrophobic. The 56º borderline for metahydrophobic and parahydrophobic materials results from the appearance of long-range attractive hydrophobic forces for higher contact angles, leading to significant changes in thin films properties (Vogler, 1998).

The contact angle is 90 degrees when a material equally well likes the gas and aqueous phases (Drzymala, 1996). It occurs when the solid/air and solid/water interfacial tensions are equal (Drzymala, 1994b).

The next range of surface hydrophobicity (90°-120°) is orthohydrophobicity. The upper border of orthohydrophobicity at 120° results from the observation that so far no material having more than 120 degrees is known (Drzymala, 2007). In the proposed here classification, extrahydrophobicity is reserved for yet-to-be discovered smooth surfaces having contact angle between 120 and 150°. Higher than 150° contact angles for materials with rough surfaces are responsible for superhydrophobicity (Onda et al., 1996; Shirtcliffe et al., 2010). Opposite to superhydrophobicity is superhydrophilicity (Onda et al., 1996, Tadanaga et al., 2010). In the proposed sub-classification of hydrophobicity and hydrophilicity, based on the concept of Drelich et al. (2011), the terms are clear and consistent with the nomenclature used in colloid and surface physical chemistry as well as flotation science and technology.

3. Materials and methods

KPF_6 (99.0%, abcr GmbH, Germany), KCl (99.5%, Chempur, Poland) and NaCl (pure for analysis, Stanlab, Poland) were used in the studies. Saturated solutions of KPF_6, NaCl and KCl were prepared basing on solubility data of Gajewska et al. (1974) and Quinn et al. (2014). The densities of saturated aqueous solutions of NaCl and KCl were taken from the handbook of Gajewska et al. (1974), while the density of the saturated KPF_6 solution was determined using a pycnometer (Dubiel, 2019). Each saturated solution was prepared by dissolving a given amount of salt in distilled water with the help of magnetic stirrer for 5 minutes at 500 rpm. The densities of NaCl and KCl were taken from CRC Handbook (1986/87) and KPF_6 from Toy (1973), while surface tensions of their saturated solutions from Weissenborn and Pugh (1996) (NaCl and KCl) and Lyklema (1995) (KPF_6).

To determine contact angles of KPF_6, KCl and NaCl the sessile drop (Adamson, 1982) and flotometry (Drzymala, 1994a) methods were used. For sessile drop experiments the investigated salt was pressed into a disc and a drop of its saturated aqueous salt solution was placed on the newly created surface. The compressed salt disks with a diameter of approximately 20 mm and a thickness of approximately 8 mm, were made of salt with a particle size <0.5 mm by means of a hydraulic press and an applied pressure of approximately 150.1 MPa. For all three salts spreading of saturated aqueous salt solution was observed, indicating contact angles equal to zero or very close to zero. The flotometric tests were carried out using the following particle size fractions: >200, 100-200, 71-100 and <71 µm. The fractions were produced using a laboratory ceramic mortar and a set of sieves. Since hardness of the salts is much smaller than that of porcelain, no cleaning the surface of the ground salts in a porcelain mortar was applied. Directly before flotometric tests, each salt sample was wetted for 2 minutes with its saturated solution and next subjected to air bubbling using a 36 cm in height Hallimond tube filled with 220 cm^3 of saturated salt aqueous suspension. The bubbling time was 30 minutes. The kinetics of the process was recorded by monitoring the yield in the calibrated Hallimond tube receiver as a function of time. The air flow was 2.5 dm^3/h. The tests were carried out at room temperature, which was 25 °C. A more detailed description of the research methodology is given elsewhere (Dubiel and Ratajczak, 2019).

The contact angle of materials can also be estimated by using the so-called flotometric equation (Drzymala, 1994a). Its simplified form (Scheludko et al., 1976), assuming that the flotation is a static process, is:

$$d_{max}/2 = \left(\frac{3\sigma}{2g(\rho_p - \rho_l)}\right)^{0.5} \cdot sin\left(\frac{\theta}{2}\right)$$

(1)

where d_{max} is the maximum size of floating particles, mm; σ surface tension, mN/m; g acceleration due to gravity, cm/s^2; ρ_p density of substance, g/cm^3, and ρ_l denotes density of aqueous solution, g/cm^3.

The flotometric equation (Eq.1) is based on a balance of forces (gravity and capillary) operating in flotation systems and relates the maximum size of floating particles d_{max} with contact angle θ and other parameters of the flotation system. The value of d_{max} can be determined from the so-called separation curve, which will be shown later, relating the maximum yield and average particle size of a tested size fraction, taking into account that $d_{max} = d_{50}$. This assumption is based on statistical considerations because d_{50} particle has an equal chance to stay in the Hallimond tube feed region as well as to be transferred to the receiver of the Hallimond tube.

To calculate the flotometric contact angle θ for the dynamic flotation conditions the following empirical equation of Kowalczuk et al. (2011) was used:

$$d_{max} = \sqrt{\frac{6\sigma}{(\rho_p - \rho_l)g}} \sin\left(\frac{\theta}{2}\right)\left(\frac{A-100}{A-141.42\sin\left(\frac{\theta}{2}\right)}\right) \qquad (2)$$

where A is a dimensionless constant reflecting the hydrodynamics of the flotation device and solid density. Parameter A from Eq. 2 can be calculated from the formula (Kowalczuk et al., 2011):

$$A_o = \frac{16A - 100\rho_p}{16 - \rho_p} \qquad (3)$$

where A_o is the dimensionless constant characterizing hydrodynamics, which was assumed in calculations to be 110, as in Hallimond tubes and laboratory mechanical flotation cells. In the equation 16 is a constant having dimension of g/cm^3. The first order kinetic constants of the performed flotation tests were calculated by using the Zuniga (1935) equation:

$$\gamma = \gamma_{max}(1 - \exp(-kt)) \qquad (4)$$

where γ is the flotation yield, %; γ_{max} maximum yield of flotation, %; k first order flotation constant, 1/min and t is the time of flotation, min.

To check how significant is the entrainment in the flotation of the investigated salts, another flotometric equation, which can be used to determine whether there is flotation or entrainment. The flotometric entrainment equation has the form (Konopacka, 2005):

$$L_x = d_{50}\left(\frac{\rho_s - \rho_w}{\rho_w}\right)^{n=0.46} \qquad (5)$$

where L_x is the flotometric entrainment constant, which for the used Hallimond tube (height 36 cm) is equal to 0.11 mm while $n = 0.46$ (Konopacka, 2005).

4. Results of investigations

The kinetics of the flotometric experiments are presented in Fig. 2. The kinetic data from Fig. 2. can be used to plot the so-called separation curves relating the maximum yield with particle size, which are shown in Fig. 3. Other experimental data and tests results are presented in Table 1.
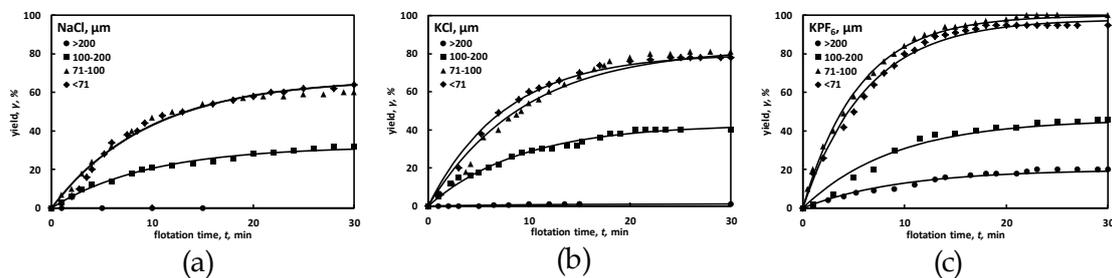
Fig. 2. Kinetics of salt flotation a) NaCl, b) KCl, c) KPF$_6$ in their saturated aqueous solutions,
depending on particle size
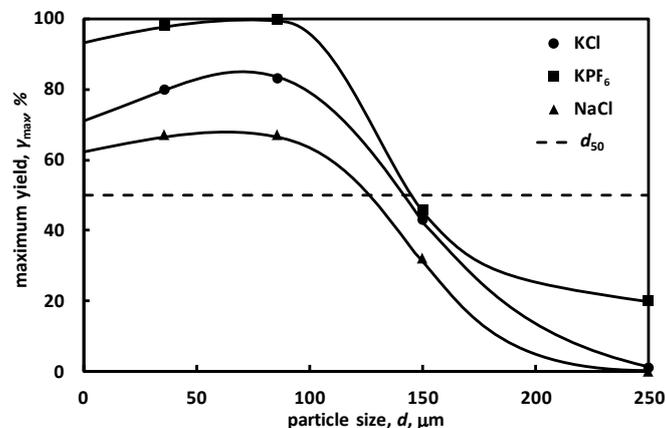
Fig. 3. Separation curves for KPF$_6$, NaCl and KCl based on data from Fig. 2. d_{50}, equal to the maximum size of floating/entrained particles d_{max}, is indicated by a dashed line

Table 1. Properties of salts and flotations tests results

Property	NaCl	KCl	KPF$_6$
Concentration of salt saturated aqueous solution, M	5.32[1]	3.74[1]	0.50[2]
Surface tension of saturated salt solutions, mN/m	84.11[3]	79.99[3]	71.50[4]
Salt density, g/cm^3	2.16[5]	1.98[5]	2.55[6]
Salt saturated solution density, g/cm^3	1.20[1]	1.16[1]	1.10[7]
Flotometric contact angle (salt/saturated solution/air, static conditions), $\theta°$	4.9	5.2	7.6
Flotometric contact angle (salt/saturated solution/air, dynamic conditions, Hallimond tube constant Ao=110), $\theta°$	4.8	5.0	6.8
Sessile drop contact angle (salt/saturated solution drop/air), $\theta°$	0[7]	0[7]	0[7]
First order kinetic constant, k, 1/min[7]			
>200	0.0010	0.0914	0.1044
100-200	0.1034	0.1088	0.1116
71-100	0.1035	0.1052	0.1810
<71	0.1023	0.1319	0.1594
Maximum yield, γ_{max}, % (after 30 min of bubbling of air)[7]			
>200	0	1	20
100-200	32	43	46
71-100	67	83	100
<71	67	80	98
Maximum size of floating/entrained particle $d_{50}=d_{max}$, µm[7]	126	141	145
Flotometric constant of entrainment for Hallimond tube 36 cm in height, L_x, µm	115[§]	116[§]	179

[1] Gajewska et al. (1974), [2] Quinn et al. (2014), [3] Weissenborn and Pugh (1996), [4] Lyklema, 1995, [5] CRC (1986/87), [6] Toy (1973), [7] Dubiel and Ratajczak, 2019, [§] for comparison: for quartz (density 2.65 g/cm^3, solution density 1 g/cm^3, d_{50} = 90 µm), magnetite (density 5.18 g/cm^3, solution density 1 g/cm^3, d_{50} = 58 µm (Konopacka, 2005)) the L_x values are 115 and 118 µm, respectively. L_x = ~116 µm (0.11 mm) indicates entrainment of particles

5. Discussion

The investigated KPF$_6$, NaCl and KCl salts appear to be hydrophilic because a drop of a saturated aqueous solution of a salt placed on the surface of the pressed disc of the salt was spreading. It shows that the contact angles are equal, or very close, to zero, meaning that they are orthohydrophilic. Extremely low contact angles of NaCl (0°) and KCl (8º) were reported by Ozdemir et al. (2009, 2011). To the knowledge of the authors of this paper the contact angle of KPF$_6$ has not been investigated previously.

The calculated flotometric contact angle was equal to about 8º for KPF$_6$ and 5° for both NaCl and KCl for the assumed static conditions of the conducted flotation tests. Similar values of the contact angles were obtained considering dynamic conditions of flotation in the used Hallimond using the device dynamic flotation constant Ao equal to 110. The small values of contact angles suggest that the investigated salts are located at the border of orthohydrophilicity and metahydrophobicity with NaCl and KCl being rather truly hydrophilic (orthohydrophilic) and KPF$_6$ being weakly hydrophobic, that is metahydrophobic. This observation is based on calculations and confirmed by the fact that KPF$_6$ is denser than KCl and NaCl and at the same time its maximum yield is greater than that of KCl and NaCl. Also, kinetic constant k (Eq. 2.) for KPF$_6$ is always greater than that of KCl and NaCl (Table 1). This also indicates that there is some flotation of KPF$_6$.

It should be noticed that the calculated flotometric contact angles were only estimated because there is always some entrainment in the Hallimond tube tests, while in the flotometric contact angle calculation the whole yield is treated as a result of flotation. This leads to overestimation of the contact

angle while underestimation of θ is a result of non-zero dynamics of flotation in the Hallimond tube and the presence of stable thin films in the case of metahydrophobic materials (θ between 0 and 56°).

It results from the tests that the value of L_x (Eq. 5) for NaCl and KCl are equal to 0.115 mm and 0.116 mm respectively, while for quartz and magnetite (Konopacka, 2005) they are 0.115 mm and 0.118 mm, respectively. It confirms that the whole observed yield of NaCl and KCl is due to entrainment. For KPF_6 L_x = 0.179 mm, being much greater than 0.11, indicating that in the used Hallimond tube, besides entrainment, there is some flotation of KPF_6.

It can be calculated from the entrainment flotometric equation (Eq. 5), for L_x = 115.5 µm as an average for entrained NaCl and KCl, that d_{50} for mechanical carryover of KPF_6 is equal to 101.7 µm. The modelled entrainment separation curve, based on d_{50} of KPF_6 equal to 101.7 µm, indicates that for instance for 100 µm particles the entrainment yield is 55%, while the experimental yield due to both flotation and entrainment is 100%. It means that for 100 µm particles the yield of true flotation of KPF_6 is 45%.

6. Conclusions

NaCl and KCl particles in their saturated aqueous solutions are orthohydrophilic and do not float while observed in the flotation test yield is a result of particles entrainment. In the case of KPF_6, besides entrainment, there is some yield due to very small metahydrophobicity of the salt. Its estimated contact angle is greater than zero but smaller than 8°. Additional flotation tests involving KPF_6 in the presence of suitable frothers may shed some light on the metahydrophobicity of this salt.

Reference

ADAMSON, A.W., 1982. *Physical chemistry of surfaces*, IV ed., Wiley, New York.

CRC, 1986/87. *Handbook of chemistry and physics*, 67th edition, CRC Press, Boca Raton, USA.

DRELICH, J., CHIBOWSKI, E., MENG, D.D., TERPILOWSKI, K., 2011. *Hydrophilic and superhydrophilic surfaces and materials*, Soft Matter 7(21), 9804-9828.

DRZYMALA, J., 1994a. *Characterization of materials by Hallimond tube flotation. Part 2: maximum size of floating particles and contact angle*, Int. J. Miner. Process., 42, 153-167 and erratum, Int. J. Miner. Process., 43, 1995, 135.

DRZYMALA, J., 1994b. *Hydrophobicity and collectorless flotation of inorganic materials*, Advances in Colloid and Interface Sci., 50, 143-186.

DRZYMALA, J., 1996. *The importance of contact angle equal to 90 degrees in interfacial processes*, Proc. International Conference on Analysis and Utilization of Oily Wastes, AUZO'96, Gdansk, Poland, 393-396.

DRZYMALA, J., 2007. *Mineral Processing. Foundations of theory and practice of minerallurgy*, Oficyna Wyd. PWr., Wroclaw, 2007, 507 pages, http://www.dbc.wroc.pl/dlibra/docmetadata? id=2070&from=publication.

DUBIEL, M., RATAJCZAK T., 2019. *Investigation of flotation of salts in their saturated solutions*, Mineral Engineering Conference MEC 2019, Poland.

GAJEWSKA, I., PIETRAS, S., RUDZINSKA, J., SCHELLENBERG, A., 1974. *Poradnik fizykochemiczny*, WNT Warszawa, Wyd. II.

KONOPACKA, Z., 2005. *Mechanical flotation*, Oficyna Wydawnicza Politechniki Wroclawskiej, Wroclaw, Poland (in Polish).

KOWALCZUK, P.B., OKTAY, S., DRZYMALA J., 2011. *Maximum size of floating particles in different flotation cells*, Minerals Engineering, 24 (766-771).

LI, Ch., SOMASUNDARAN, P., 1993. *Role of electrical double layer forces and hydrophobicity in coal flotation in NaCl solutions*. Energy & Fuels, 7, 244-248.

LIPNIARSKI, M., RATAJCZAK, T., DRZYMALA, J., 2015. *Weryfikacja hipotez o roli soli we flotacji na przykladzie wegla kamiennego w wodnych roztworach NaCl i KPF$_6$*, III Polski Kongres Gorniczy, Mineralurgia i wykorzystanie surowcow mineralnych (WGGG PWr, Wroclaw), 35–9.

LYKLEMA, J., 1993. *Fundamentals of interface and colloid science. Vol. 1, Fundamentals*, Academic Press, London.

LYKLEMA, J., 1995. *Fundamentals of interface and colloid science. Vol. 2. Solid-liquid interfaces*, Academic Press, London, p. 3.178.

MILLER, J. D., YALAMANCHILI, M. R., and KELLAR, J. J., 1992. *Surface charge of alkali halide particles as determined by laser-Doppler electrophoresis*, Langmuir 8 (1992) 1464-69.

ONDA, T., SHIBUICHI, S., SATOH N., TSUJII, K. 1996. *Super-water-repellent fractal surfaces*, Langmuir 12(9), 2125-2127.

OZDEMIR, O., DU, H., KARAKASHEV, S.I., NGUYEN, A.V., CELIK, M.S., MILLER, J.D., 2011. *Understanding the role of ion interactions in soluble salt flotation with alkylammonium and alkylsulfate collectors*, Advances in Colloid and Interface Science 2011;163(1):1-22.

OZDEMIR, O., KARAGUZEL, C., NGUYEN, A.V., CELIK, M.S., MILLER, J.D., 2009. *Contact angle and bubble attachment studies in the flotation of trona and other soluble carbonate salts*. Minerals Engineering, 22(2),168-175.

QUINN, J.J., SOVECHLES, J.M., FINCH, J.A., WATERS, K.E., 2014. *Critical coalescence concentration of inorganic salt solutions*, Minerals Engineering 58, 1-6.

RATAJCZAK, T., DRZYMALA, J., 2003. *Salt flotation*, Oficyna Wydawnicza Politechniki Wroclawskiej, Wroclaw, Poland (in Polish).

SCHELUDKO, A., TOSHEV, B.V., BOJADJIEV D.T., 1976. *Attachment of particles to a liquid surface (capillary theory of flotation)*, Faraday Trans. I. 12 pp 2815-2828.

SHIRTCLIFFE, N.J., MCHALE, G., ATHERTON, S., NEWTON, M.I., 2010. *An introduction to superhydrophobicity*, Advances in Colloid and Interface Science, Volume 161, Issues 1–2, 15 December 2010, p. 124-138.

TADANAGA, K., MORINAGA, J., MATSUDA, A., MINAMI, T., 2000. *Superhydrophobic-superhydrophilic micropatterning on flowerlike alumina coating film by the sol-gel method*, Chemistry of Materials, 12(3), 590-592.

TOY, A.D.F., 1973. *The chemistry of phosphorous*, Pergamon texts in inorganic chemistry, V. 3., Pergamon Press, Oxford, p. 537.

VOGLER, E.A., 1998. *Structure and reactivity of water at biomaterial surfaces*, Advances in Colloid and Interface Science, 74, 69-117.

WEISSENBORN, P.K., PUGH, R.J., 1996. *Surface tension of aqueous solutions of electrolytes: relation with ion hydration, oxygen solubility, and bubble coalescence,* J. Coll. Interface Sci., 184, 550-563.

ZUNIGA, H.G., 1935. *Flotation recovery is an exponential function of its rate*. Boln. Soc. Nac. Min., Santiago, Chile, 47, 83-86.