

Załącznik 4

**AUTOREFERAT
PRZEDSTAWIAJĄCY OPIS
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NAUKOWYCH
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AUTOPRESENTATION

1. Name and surname

Przemysław Bogusław Kowalczyk

2. Diplomas held and scientific degrees

a) Master of Science (M.Sc.)

2008, Wrocław University of Technology, Faculty of Fundamental Problems of Technology

Field of study: materials engineering

Specialization: chemical metallurgy and corrosions of metals

Professional degree obtained: Master of Science

Thesis title: *Chemical and mineralogical changes in non-oxidative and atmospheric leaching of shale fraction of copper ore*

Supervisor: Dr. Tomasz Chmielewski

Reviewer: Prof. Władysław Walkowiak

b) Doctor of Philosophy (Ph.D.)

2012, Wrocław University of Technology, Faculty of Geoengineering, Mining and Geology

Field of study: mining and geological engineering

Specialization: minerals engineering, materials engineering, physicochemistry of surfaces

Professional degree obtained: doctor of philosophy

Thesis title: *Theoretical and experimental determination of the maximum size of floating particles in different devices*

Supervisor: Prof. Jan Drzymała

Reviewers: Dr. Andrzej Łuszczkiewicz, Prof. Marian Brożek

c) Mining degree

Mining Director of 3rd level – granted by the Minister of Economy of Poland, November 6, 2014

3. Information on employment in scientific institutions

a) employment

06.2007 – 10.2007, Wrocław University of Technology, Faculty of Chemistry, laboratory technician

02.2008 – 09.2008, Wrocław University of Technology, Institute of Mining, chemist

02.2012 – 09.2012, University of Exeter, Camborne School of Mines, research assistant

10.2012 – 09.2013, Wrocław University of Technology, Faculty of Geoengineering, Mining and Geology, Institute of Mining, assistant

10.2013 – until now, Wrocław University of Technology, Faculty of Geoengineering, Mining and Geology, Department of Mineral and Waste Processing, assistant professor

11.2015– until now, Wrocław University of Technology, Faculty of Geoengineering, Mining and Geology, Department of Mineral and Waste Processing, Vice-Head of Department

b) internships

1) University of Exeter, Camborne School of Mines, UK, research assistant 02-09.2012

2) Stanford University, Stanford Centre for Professional Development, US, visiting scholar, 10.2013 – 12.2013

3) Dumlupinar University, Faculty of Engineering, Turkey, Teaching staff mobility, visiting scientist, 2013 – until now

4) Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Krakow, Poland, visiting scientist, 2015 – until now

4. Indication of accomplishment resulting from art. 16 sec. 2 of the Act of March 14, 2003 on academic degrees and academic titles and on art degrees and titles (Journal of Laws no. 65, item 595 as amended)

a) academic accomplishment

The basis of applying for scientific degree of habilitation (*doktor habilitowany*, D.Sc.) is a collection of ten scientific papers indexed by the Journal Citation Reports (JCR) under common title:

Physicochemical aspects of flotation of naturally hydrophobic substances.

b) Author/authors, publication title/titles, year, publisher

Publications are listed in the same order as they are discussed in the autopresentation.

[H1] **Kowalczyk P.B.** *Determination of critical coalescence concentration and bubble size for surfactants used as flotation frothers.* Ind. Eng. Chem. Res., 2013, 52(33), 11752–11757 (IF 2.235, MNiSW 35)

Single author.

[H2] **Kowalczyk P.B.**, Drzymala J. *Physical meaning of the Sauter mean diameter of spherical particulate matter*. Part. Sci. Technol., 2016 (doi: 10.1080/02726351.2015.1099582) (IF 0.523, MNiSW 15)

My contribution to this work consisted of participating in defining the scientific problem, determination of physical meaning of the Sauter mean diameter, interpretation and discussion of results, manuscript preparation and revision after referee comments. Estimated percentage of my contribution is 80%.

[H3] **Kowalczyk P.B.**, Drzymala J. *Some remarks on attachment of a gas bubble to another phase both immersed in a water*. Physicochem. Probl. Miner. Process., 2016, 52(1), 147-154 (IF 0.926, MNiSW 20)

My contribution to this work consisted of participating in defining the scientific problem, interpretation and discussion of results, manuscript preparation and revision after referee comments. Estimated percentage of my contribution is 75%.

[H4] Janicki M., Drzymala J., **Kowalczyk P.B.** *Structure and surface energy of both fluorite halves after cleaving along selected crystallographic planes*. Physicochem. Probl. Miner. Process., 2016, 52(1), 451-458 (IF 0.926, MNiSW 20)

My contribution to this work consisted of co-participating in development of research plan, interpretation and discussion of results, literature survey, manuscript preparation and revision after referee comments. Estimated percentage of my contribution is 40%.

[H5] **Kowalczyk P.B.** *Flotation and hydrophobicity of quartz in the presence of hexylamine*. Int. J. Miner. Process., 2015, 140, 66–71 (IF 1.310, MNiSW 25)

Single author.

[H6] **Kowalczyk P.B.**, Zawala J., Drzymala J., Malysa K. *Influence of hexylamine on kinetics of flotation and bubble attachment to the quartz surface*. Sep. Sci. Techn. 2016 (doi: 10.1080/01496395.2016.1172640) (IF 1.171, MNiSW 25)

My contribution to this work consisted of co-participating in defining the scientific problem, conduction of experiments, interpretation and discussion of result, manuscript preparation and revision after referee comments. Estimated percentage of my contribution is 60%.

[H7] **Kowalczyk P.B.**, Buluc B., Sahbaz O., Drzymala J. *In search of an efficient frother for pre-flotation of carbonaceous shale from the Kupferschiefer stratiform copper ore*. Physicochem. Probl. Miner. Process., 2014, 50(2), 835–840 (IF 0.926, MNiSW 25)

My contribution to this work consisted of co-participating in defining the scientific problem, conduction of experiments, interpretation and discussion of result, manuscript preparation and revision after referee comments. Estimated percentage of my contribution is 55%.

[H8] **Kowalczyk P.B.**, Zaleska E., Danczak O. *Flotation of carbonaceous copper shale-quartz mixture with poly(ethylene glycol) alkyl ethers*. Trans. Nonferrous Met. Soc. China, 2015, 25(1), 314-318 (IF 1.178, MNiSW 35)

My contribution to this work consisted of participating in development of research plan, interpretation and discussion of results, literature survey, manuscript preparation and revision after referee comments. Estimated percentage of my contribution is 60%.

[H9] **Kowalczyk P.B.**, Mroczo D., Drzymala J. *Influence of frother type and dose on collectorless flotation of copper-bearing shale in a flotation column*. Physicochem. Probl. Miner. Process., 2015, 51(2), 547-558 (IF 0.926, MNiSW 20)

My contribution to this work consisted of co-participating in defining the scientific problem, conduction of experiments, interpretation and discussion of result, manuscript preparation and revision after referee comments. Estimated percentage of my contribution is 65%.

[H10] **Kowalczyk P.B.**, Zawala J., Kosior D., Drzymala J., Malysa K. *Three phase contact formation and flotation of highly hydrophobic polytetrafluoroethylene in the presence of increased dose of frothers*. Ind. Eng. Chem. Res., 2016. 55(3), 839–843 (IF 2.587, MNiSW 35)

My contribution to this work consisted of conducting, interpretation and discussion of result, manuscript preparation and revision after referee comments. Estimated percentage of my contribution is 40%.

c) description of the objective of the aforementioned papers and academic accomplishment achieved

Flotation is a physicochemical process commonly used for upgrading of ores and other materials. Flotation is used to separate valuable substances from unwanted ones utilizing differences in their surface properties. In flotation, hydrophobic substances having the water contact angle greater than zero, attach to gas bubbles, form stable particle-bubble aggregates and move upwards to either the froth layer (froth flotation) or the liquid/gas interface (surface flotation) where they are collected as a concentrate, while the hydrophilic or slightly hydrophobic substances do not attach to gas bubbles and sink.

Flotation is a complex process and its complete description is very difficult because it may require more than 100 parameters. The efficiency of flotation depends on many parameters including: *i*) properties of floating substances, that is their hydrophobicity, size, density, surface charge; *ii*) type, construction and hydrodynamics of flotation devices; *iii*) mode of work, including type and dose of flotation reagents, surface tension of liquid, size of gas bubbles, pH, electrochemical potential of solution and many others. Any change in flotation parameters causes variations in the whole process. Therefore, the selection of proper parameters is crucial to make the process highly effective both in laboratory and industrial scales.

The aim of my academic accomplishment, presented in a series of ten scientific publications entitled as *Physicochemical aspects of flotation of naturally hydrophobic substances*, was to determine the influence of selected parameters on the flotation process. The presentation of the accomplishment is divided into several parts. The first one was performed to establish a better

understanding of the role of frothers in flotation, particularly their influence on the gas bubble size and prediction of the critical coalescence concentration basing only on the chemical structure of the frothers. The next part concerned the hydrophobicity, structure and property of newly created surfaces formed by cleaving along selected planes. The essential goal of the study was to show the mechanism of flotation and three-phase contact formation of naturally hydrophobic substances with different degrees of hydrophobicity, that is slightly hydrophobic quartz, moderate hydrophobic fluorite and carbonaceous copper-bearing shale, and highly hydrophobic polytetrafluoroethylene (Teflon®). The description of the mechanism was possible due to comparison of the kinetics of the three-phase contact formation, determined from the single bubble tests, with flotation kinetics in devices with different hydrodynamics.

Frothers: Bubble size and critical coalescence concentration

Frothers play a crucial role in flotation. The type and dose of frothers determine the bubble size, and hence the efficiency of flotation [1-3]. Frothers reduce bubble size, prevent bubble coalescence, stabilize the froth layer and shorten the time of three-phase contact formation. The mean bubble size formed mechanically and in capillaries decreases with frother concentration and coalescence is prevented at the critical coalescence concentration CCC [1]. This trend is observed for all flotation frothers providing different values of CCC. The value of CCC is very useful in determining the concentration (dose) at which flotation should be conducted. The critical coalescence concentration is difficult to estimate since it has different values depending on definitions. The general definition of CCC_x is expressed as [H1]:

$$CCC_x = (d_{\max} - d_{\min}) \cdot (1 - x/100) + d_{\min} \quad (1)$$

where x means percent reduction of the bubble size from a maximum value in water d_{\max} to a minimum level in the presence of frother d_{\min} . For instance CCC_0 means that no frother is used and bubbles reach the maximum size d_{\max} , CCC_{50} indicates that only 50% of bubble size is reduced, while CCC_{100} means that the bubble coalescence is completely prevented and the bubble size is at minimum (d_{\min}).

There are many ways and formulas for expressing the mean bubble size. One of many possible formulas is the Sauter mean diameter also called the surface-volume mean d_{32} . An analysis of numerous papers and book dealing with particulate matter indicated that the physical meaning of the Sauter mean diameter of polydispersed objects was not known. During my study I derived and presented a physical meaning of the Sauter mean diameter [H2]. It was proved that the Sauter mean diameter of a collection of spherical objects of different sizes is equal to the diameter of equisized spherical objects forming a collection (Fig. 1). The polysized and equisized systems have different numbers of spherical objects, identical total surface area, and identical total volume. If the surface

energy of all spheres of both systems is the same, they can be called equienergetic. This equivalence provides the physical meaning of the Sauter mean diameter and is equal to:

$$d_{32} = \left(\frac{\sum_{i=1}^n n_i d_i^3}{\sum_{i=1}^n n_i d_i^2} \right). \quad (2)$$

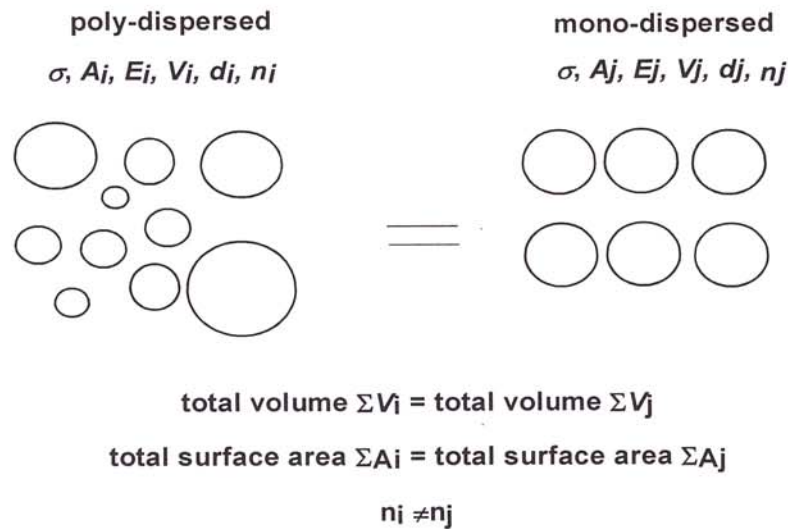


Fig. 1. Physical meaning of the Sauter mean diameter d_{32} [H2]

Surfactants used as flotation frothers are characterized by different parameters including molecular weight (MW), hydrophilic-lipophilic balance (HLB), critical coalescence concentration (CCC), dynamic foamability index (DFI), dynamic stability factor (DSF), maximum recovery (ϵ_{\max}) and others. In the liquid/gas phase system frothers are classified into selective and powerful. Powerful frothers have low values of CCC and high of DFI, HLB and MW, while selective ones have high values of CCC and HLB and low DFI and MW [4]. According to Laskowski [4] the powerful frothers create more stable foam and can be used for flotation of coarse particles, while the selective frothers are used for separation of fine particles.

Many studies have been conducted to find a relationship between two or more parameters characterizing flotation frothers. However, so far no satisfying correlation has been given. In my work, basing on experimental data published in literature [3,5], I showed that there is a strong correlation between the critical coalescence concentration (CCC) and the ratio of hydrophilic-lipophilic balance (HLB) to molecular weight (MW) for 29 frothers with known chemical structure (Fig. 2) [H1], that is for aliphatic alcohols ($C_nH_{2n+1}OH$), propylene glycol ethers frothers ($C_nH_{2n+1}(OC_3H_6)_mOH$), polypropylene glycols ($H(OC_3H_6)_mOH$) and nine commercial frothers. The proposed in my work empirical model allows, with relatively high determination coefficient of $R^2=0.97$, to predict the values of critical coalescence concentration CCC_{95} based only on the chemical

structure of the frother, that is hydrophilic-lipophilic balance (HLB) and molecular weight (MW) [H1]:

$$CCC_{95} = \frac{209,71 \cdot (HLB/MW)}{105,14 - 800 \cdot (HLB/MW)} \quad (3)$$

The proposed equation is universal for all tested in my work frothers.

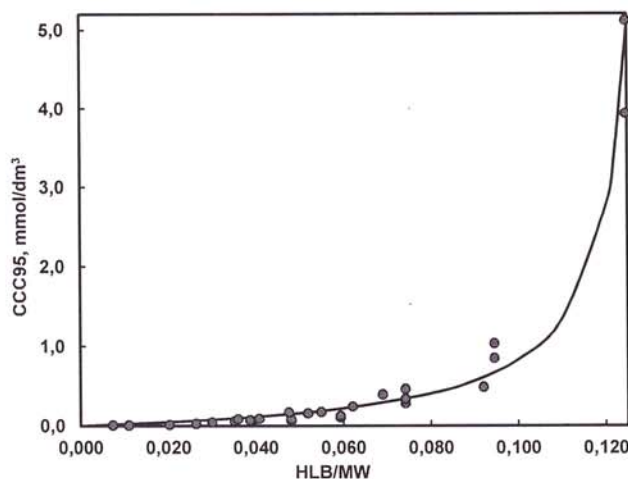


Fig. 2. The CCC_{95} vs. HLB/MW correlation for aliphatic alcohols, propylene glycol ethers frothers, polypropylene glycols and commercial frothers [H2]

In the same paper [H1] I determined a new relationship between normalized bubble size $(d_{32}-d_{\min})/d_{\max}$ and normalized frother concentration C/C_{\max} which can be used to model the influence of frother concentration on the Sauter mean bubble size d_{32} :

$$d_{32} = (d_{\max} - d_{\min}) \frac{(1 - C/C_{\max}) \cdot (F - 100)}{(F - 100 \cdot C/C_{\max} - 100)} + d_{\min} \quad (4)$$

where parameter F is applied for relating d_{32} and concentration C and can be called the frother concentration empirical constant, while C_{\max} stands for the maximum concentration of frother when the bubble size is minimum d_{\min} . The obtained empirical model can be used to predict the Sauer mean bubble size d_{32} for any flotation frother.

Hydrophobicity of substances

Hydrophobicity of substances is the most significant factor affecting the time of three phase contact formation, and thus flotation kinetics. Hydrophobicity of a solid/gas/water system can be characterized by the so-called contact angle responsible for the appearance of a capillary force, the main force of bubble-to-surface adhesion. The term hydrophobicity indicates that the three-phase contact angle of the solid/gas/liquid system, measured through the aqueous phase, is greater than 0 degrees, while the system is referred to as hydrophilic when the contact angle is zero [H3].

Hydrophobicity alone does not affect the flotation process. Another important parameter is the interfacial liquid film which allows for attachment of bubble to either hydrophobic solid surface. The three-phase contact formation, and thus attachment occurs only when the interfacial liquid film between bubble and floating substance is ruptured. In the case of naturally hydrophobic substances the attachment occurs not spontaneously but with a certain rate due to repulsions caused by the aqueous films formed between the air bubble and substance (particle, oil drop etc.) [H3]. The mechanism of interactions between the bubble and solid surfaces will be shown and discussed later.

Prior to each separation process, the solid substances are crushed and ground in order to obtain a certain particle size and to release useful components from the gangue. Comminution of solid substances produces completely new surfaces which can exhibit not necessarily identical properties such as arrangement of surface ions, surface charge and hydrophobicity. In my work I conducted theoretical and experimental considerations on the surface properties of minerals after cleaving them along certain planes. The structure of newly created surfaces of fluorite and their surface energies were examined and theoretically calculated taking into account surface ions reorganizations [H4]. I also experimentally determined the advancing and receding contact angles by the sessile drop method for fluorite, calcite and mica (my study, unpublished data).

Fluorite is a semi-soluble salt and it has been of great interest in many applications. Pure fluorite can be considered as either hydrophilic or hydrophobic mineral with the water contact angle either equal or greater than zero, respectively. Fluorite cleaves along three planes, that is (111), (110) and (100). Splitting of fluorite along these planes creates new surfaces which can be either identical or different (Fig. 3). The quantum-mechanical calculations allowed to determine the surface energies of fluorite planes after cleavage (Table 1).

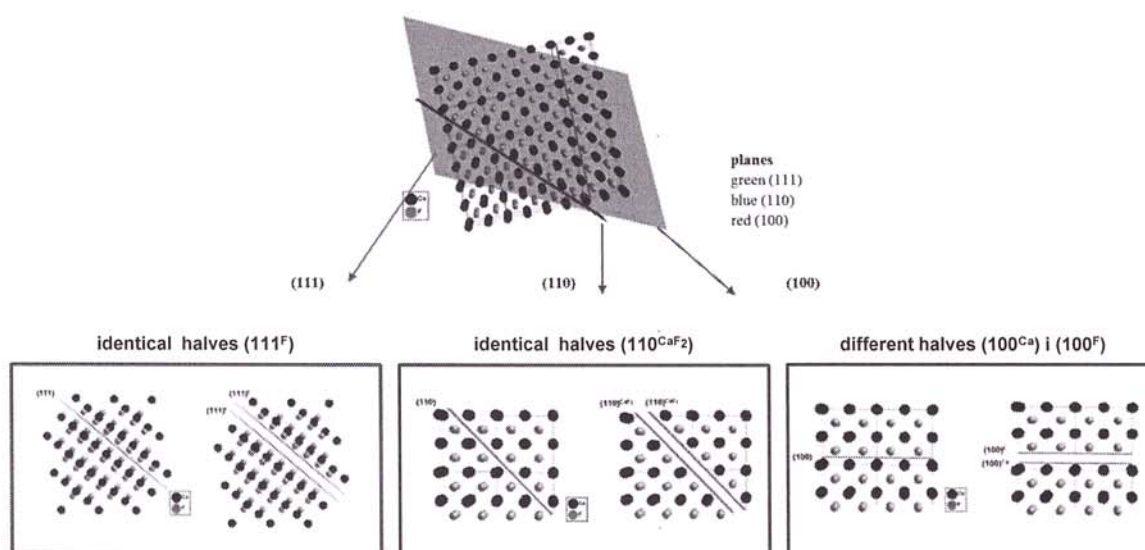


Fig. 3. Surface structures of fluorite split into halves along (111), (110) and (100) planes (based on [H4])

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Table 1. Calculated surface energies and relaxation of ions forming different surfaces of fluorite [H4]

Cleavage plane	Surface energy, J/m ² calculated	Surface energy, J/m ² literature data[7]	Relaxation, %
(111 ^F)	0.384	0.392	1.04
(110 ^{CaF₂})	0.723	0.613	1.78
(100 ^{Ca})	0.866	0.840	2.82
(100 ^F)	0.458	n/a	3.51

Splitting a piece of fluorite along (111) plane provides two identical surfaces which consist of only F ions (111F) (Fig. 3). The relaxation of surface ions forming the surface is not significant because the change of Ca-F bond length is close to 1% (Table 1). The presence of only fluoride ions suggests that the newly created surfaces are hydrophobic.

Similar situation occurs for the (110) plane (Fig. 3). In this case both surfaces after cleavage contain fluoride and calcium ions (111^{CaF₂}) at the same proportion 2:1 as in the CaF₂ molecule. It suggests that the newly created surfaces, with the relaxation of surface ions less than 2%, can exhibit either hydrophobic (presence of fluoride ions) or hydrophilic (presence of calcium ions) properties.

The situation is different in the case of fluorite (100) plane (Fig. 3). Splitting along the (100) plane leads to two completely different surfaces. One of them consists of calcium (100^{Ca}), while the second one of fluoride (100^F) ions. The surface energy of the half covered with the Ca ions (100^{Ca}) is equal to 0.866 J/m², while the surface energy of the second half with the fluoride atoms (100^F) is 0.458 J/m² (Table 3) Thus, there is a significant difference in the surface energies of the created halves. As a result, it should be expected that the hydrophobicity of both halves can be different. Perhaps, the difference in the contact angles of fluorite (100) plane observed by Zhang et al. [8] (0°) and by Gao et al. [9] (32°) was caused by measuring contact angle not for the same but for the corresponding halves.

Theoretical considerations of the physicochemical structure of materials and their cleavage planes indicated that either splitting, fracturing or cleavage of a piece of mineral into halves provided two new surfaces, which can be either identical or unequal. In order to verify the theoretical considerations I conducted the experiments which allow to determine the advancing and receding contact angles measured by the sessile drop technique, for fresh surfaces obtained by mechanical splitting of fluorite, calcite and mica into halves. The presented in Table 2 results of contact angle measurements show that there is no difference in the receding (1st half 26±4°, 2nd half 27±4°) and advancing (1st half 90±3°, 2nd half 90±2°) contact angles for the corresponding surfaces of fluorite obtained by splitting a piece of the mineral into halves. It suggests that splitting of

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fluorite was along (111) or (110) planes (Fig. 3). Table 2 also shows that fluorite is a naturally hydrophobic mineral since its advancing and receding contact angles are greater than zero. The relatively high values of contact angles suggest that fluorite was cleaved along (111) plane with fluoride ions on the surface (111^F).

Table 2. Mean advancing and receding contact angles of the investigated minerals (unpublished data)

	1 st half		2 nd (corresponding) half	
	advancing, °	receding, °	advancing, °	receding, °
fluorite	90±3	26±4	90±2	27±4
calcite	77±3	27±5	78±3	29±6
mica	46±3	17±2	50±3	18±2

The data presented in Table 1 show that there is no difference in the advancing and receding contact angles on corresponding surfaces of calcite and mica after splitting. It proves that splitting of calcite along its perfect cleaving plane provides two identical (10T4) surfaces which contain both Ca^{2+} and CO_3^{2-} ions in the same layer. Also two surfaces obtained by cleaving mica along the (001) plane, which is the perfect cleaving plane, are always identical.

Flotation of slightly hydrophobic quartz in water and in the presence of hexylamine

The knowledge of surface properties of substances allows to explain the mechanism of their flotation in water and in the presence of various surfactants. Solid substances can be either hydrophobic or completely wetted by water. Quartz, similarly to fluorite, is generally considered to be a hydrophilic or slightly hydrophobic mineral with the water contact angle greater than zero. During my study I confirmed that quartz exhibits hydrophobic properties since its rest contact angle measured by the sessile drop technique on the flat and polished surface is greater than zero and is equal to 20° [H5, H6].

Although quartz exhibits native hydrophobicity, it does not float in pure water in the tested range of pH shown in Fig. 4. A lack of quartz flotation (Fig. 4) and TPC formation (Fig. 5) in pure water does not result from its hydrophilicity but from stability of the interfacial water film separating the bubble and quartz surfaces. In pure water, both surfaces of quartz and bubble are negatively charged and the repulsive electrostatic interactions prevent the film rupture and formation of a stable particle-bubble aggregate [H6].

According to many investigations, flotation of quartz is only possible by using collectors, which render quartz hydrophobic. The value of contact angle of quartz strongly depends on the collector dose and type as well as pH of solution. The most common collectors used in flotation of quartz are long chain alkyl amines, especially dodecylamine [10,11]. There are only a few papers which

discuss the influence of short chain alkyl amines on the flotation performance and hydrophobicity of quartz [10, 12]. In my work I showed that hexylamine (HexNH_2) as an example of short chain alkyl amine, plays a role of collector and frother in flotation [H5, H6]. Flotation kinetics and time of three-phase contact formation depend on HexNH_2 concentration and pH of the solution (Figs. 4-6). The presence of amine destabilizes the interfacial liquid film between the bubble and quartz surfaces leading to the formation of the three-phase contact, and thus stable particle-bubble aggregate. The mechanism of TPC formation was described in the paper on *Influence of hexylamine on kinetics of flotation and bubble attachment to the quartz surface* abbreviated as [H6].

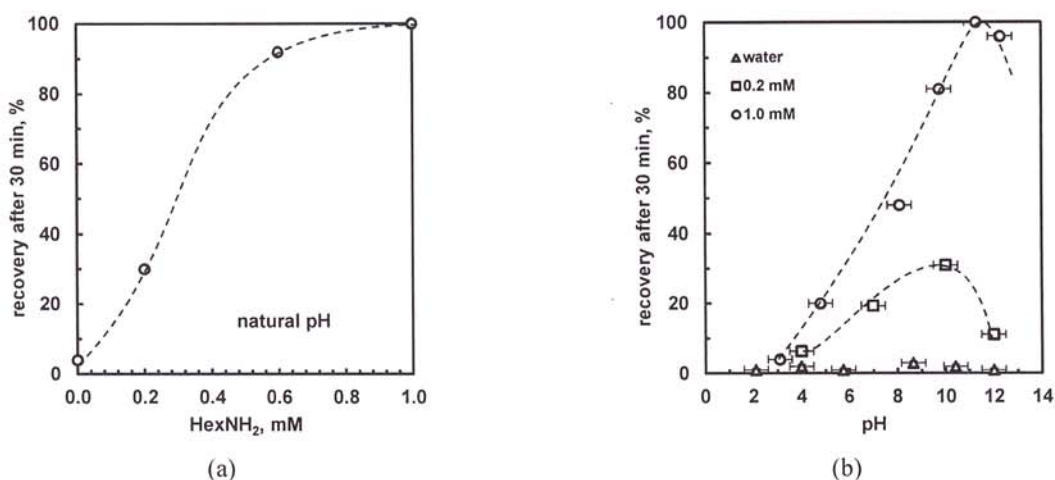


Fig. 4. Influence of (a) concentration and (b) pH of aqueous solutions of HexNH_2 on recovery of quartz after 30 minutes of flotation [H5, H6]

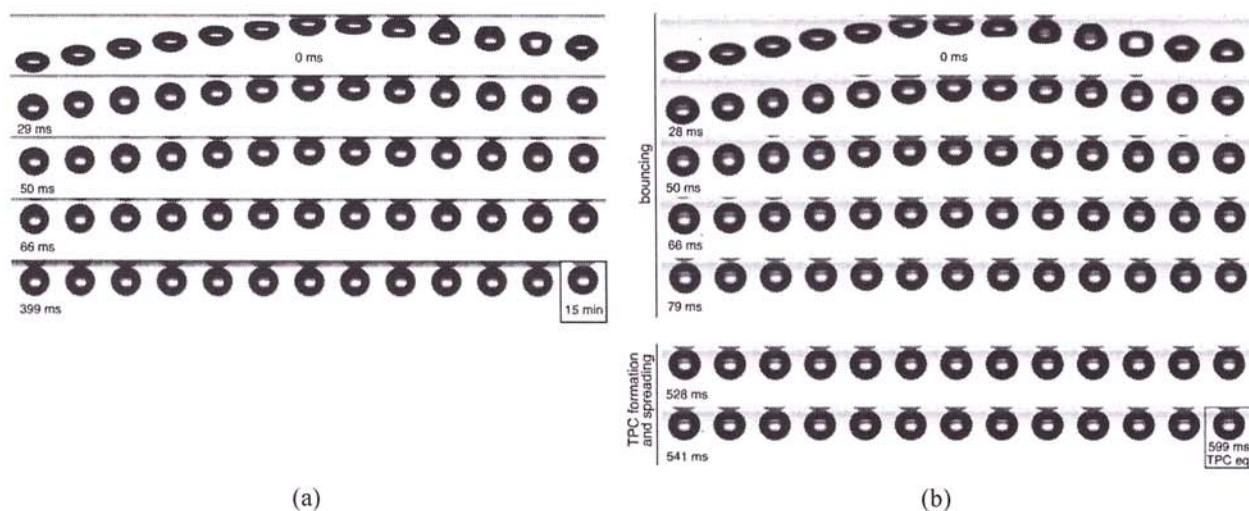


Fig. 5. Sequences of photos of the bubble colliding with the quartz surface in (a) pure water (pH 5.8) and (b) in $2 \cdot 10^{-4}$ M HexNH_2 solutions (pH 5.8) [H6]

I showed that there is a strong correlation between flotation kinetics, expressed as the inversed first order rate constant k^{-1} , and time of three-phase contact formation t_{TPC} determined from the

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single bubble tests. Figure 6 shows that both values of t_{TPC} and $1/k$ strongly depend on pH of the aqueous solution of hexylamine. It can be clearly seen that with increasing pH of aqueous solution of HexNH_2 , the values of $1/k$ and t_{TPC} decreased to a certain point, and then increased.

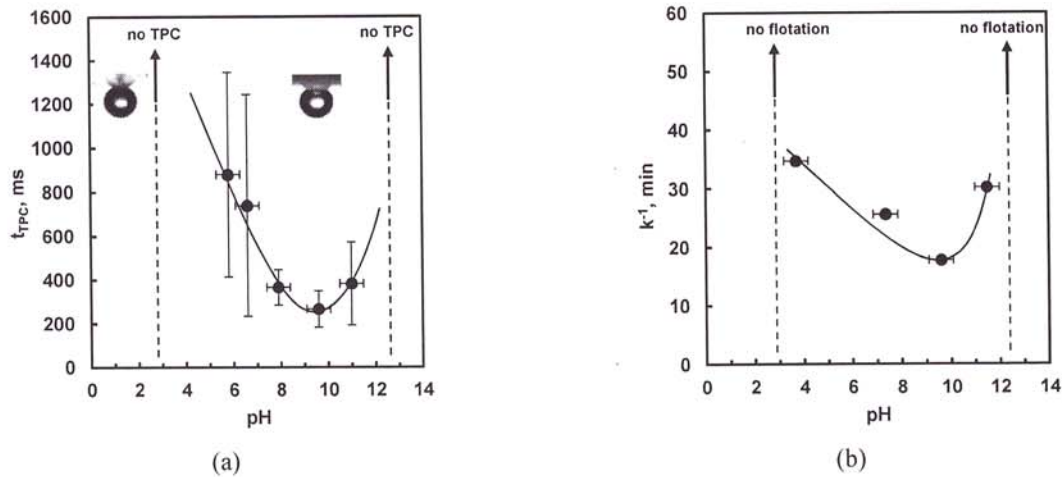


Fig. 6. Influence of pH of $2 \cdot 10^{-4}$ M HexNH_2 aqueous solution on (a) values of t_{TPC} determined from the single bubble tests and (b) inverted values of the kinetics constant k^{-1} determined from the flotation tests [H6]

The best results of flotation and single bubble flotation tests were obtained at alkaline solutions at pH equal to 9.6, while below and above this pH, the recovery of quartz decreased and values of $1/k$ and t_{TPC} increased. It can be attributed to adsorption of amine ions on both bubble and quartz surfaces which causes electrostatic/repulsive interactions leading to destabilization/stabilization of the interfacial liquid film. Adsorption of amine ions on the quartz surface, which slightly improves quartz hydrophobicity from 23 to 34°, can destabilize the liquid film between bubble and quartz due to the nucleation mechanism [H6]. Adsorption of positively charged amine ions can cause reversal of the bubble surface charge from negative to positive. It means that in the thin liquid film, separating the bubble and quartz surfaces, the attractive electrostatic forces start to operate and they cause film destabilization and rupture. The type of adsorbed ions strongly depends on the pH of amine. At pH equal to the dissociation constant pK_a the concentrations of ionized and neutral species of amines are equal. The change in pH results in a change of the neutral-to-ionized species ratio. The best results were observed below and close to $\text{pH} = \text{pK}_a$, which is equal to 10.56, as a result of co-adsorption of ionized (RNH_3^+) and neutral species (RNH_2). A sharp increase in the values of t_{TPC} and k^{-1} above $\text{pH} = \text{pK}_a$ can be explained by precipitation of amine. The fine species of precipitating amines, in the form of neutral species, are highly surface active, coat the surface of quartz and form molecular monolayer film at the liquid/gas interface preventing the particle-bubble attachment.

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Flotation of moderate hydrophobic fluorite and carbonaceous copper-bearing shale

The presented hitherto theoretical and experimental considerations showed that fluorite is naturally hydrophobic mineral. The single bubble flotation tests showed that investigated in this work pure fluorite exhibited moderate hydrophobic properties with water advancing contact angle equal to 40° (Kowalczyk and Zawala, unpublished data). The natural hydrophobicity of fluorite indicates that it exhibits native floatability and can be easily floated without any surfactant in small flotation devices such as Hallimond tube and Schott funnel [13, 14]. However, the flotation response and bubble attachment strongly depend on pH of solution (Fig. 7, Kowalczyk and Zawala, unpublished data). Similarly to slightly hydrophobic quartz, also for fluorite there is a strong correlation between the t_{TPC} and $1/k$ values. The values of $1/k$ and t_{TPC} are highly correlated and changing similarly within the same range of pH (Fig. 8).

As seen in Figures 7 and 8, the lowest recoveries and the highest values of t_{TPC} and $1/k$ are observed at strongly acidic and basic pH, respectively, while the best results are obtained at pH 6-8. It corresponds well to the values of either point of zero charge or isoelectric point of fluorite. At pH 2.6 both surfaces of fluorite and bubble are positively charged, whereas at pH 11 are negatively charged [15, 16]. At pH 5.8 positively charged fluorite can be electrostatically attached to the electronegative bubble. A lack of flotation and bubble attachment at the acidic and basic pH values indicate the repulsive electrostatic interactions, which prevent rupture of the interfacial liquid film formed between the bubble and fluorite surfaces. Increasing pH from 2 to 6 enhances the flotation rate and recovery. Also the t_{TPC} is shortened with increasing pH (Fig. 4).

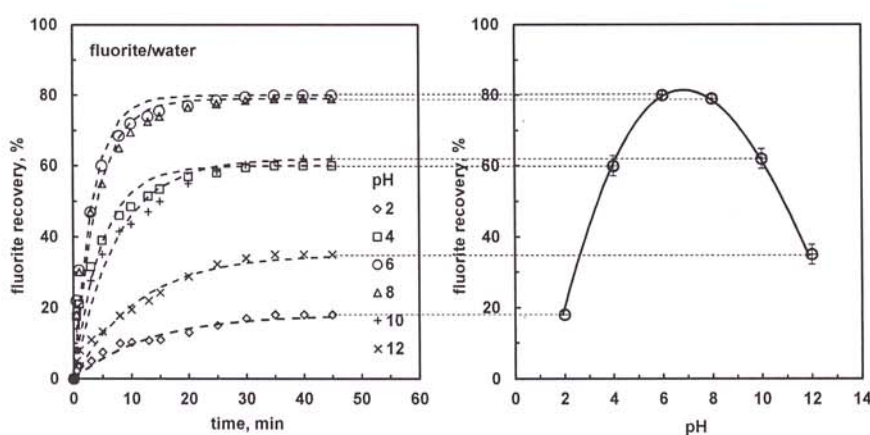


Fig. 7. Flotation recovery of fluorite as a function of pH

The surface charge of fluorite originates from dissolution of F^- and Ca^{2+} ions from the surface. The surface charge is very high at low pH and decreases with increasing pH. It is attributed to specific adsorption of OH^- ions on the fluorite surface and possible randomization of water molecules on the surface at pH close to pzc [17]. At higher pH, there is strong adsorption of OH^-

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ions and formation of Ca-OH. Adsorption of OH⁻ on the fluorite and bubble surfaces increases their negative charges densities and decrease the surface charge. It leads to dissociative adsorption of water molecules on the CaF₂ surface, and therefore the surface hydrophilization.

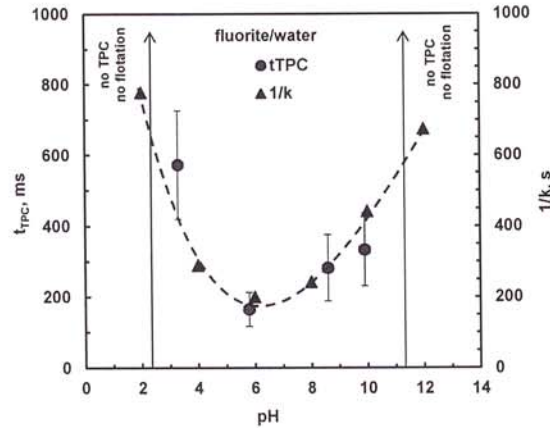


Fig. 8. Dependencies of t_{TPC} (ms) values, determined from the single bubble tests and inversed values of the kinetics constant $1/k$ determined from the flotation tests, on pH of solution, for the fluorite/water system (Kowalczyk and Zawala, unpublished data)

The second investigated moderate hydrophobic solid was carbonaceous copper-bearing shale originated from the Kupferschiefer stratiform copper ore (Legnica-Glogow Zechstein Copper Basin LGOM). Carbonaceous copper-bearing shale, together with dolomitic and sandstone lithological layers forms the copper ore. Interesting geochemical and petrological properties, as well as relatively high content of copper and other elements (Table 3), cause that shale is an important technological component. On the other hand, a high content of organic carbon and hydrocarbons causes a number of technological problems in all stages of copper ore processing, including flotation and refining [18]. Therefore, different actions and methods are aimed to reduce the content of organic carbon occurring in the structure of shale in the form of hydrophobic organic compounds such as kerogen, bitumen and graphite. One of many possible methods is collectorless flotation in the presence of frothers only. Such a method in industry is also called pre-flotation. During my research work I conducted a series of studies to establish a better understanding of shale behavior in water and in the presence of frothers. I described the role of frothers in collectorless flotation of naturally hydrophobic substances such as carbonaceous copper-bearing shale [H7, H8, H9].

Carbonaceous copper-bearing shale from LGOM is naturally hydrophobic polymineral and polymetallic substance with the water contact angle greater than zero. The advancing and receding contact angles for the investigated shale/water/air system measured by the sessile drop technique were 30 and 40 degrees, respectively [21]. The measurements of rest contact angle showed that the hydrophobicity of shale only slightly depended on pH [22]. The addition of frothers did not change the natural hydrophobicity of shale [21]. The natural hydrophobicity of investigated shale indicates

that it may exhibit native floatability. Figure 9 shows the flotation results in pure water (frother concentration 0) and in the presence of nonionic frothers. When shale was floated in water, its recovery was practically zero. Addition of frothers initiated flotation of shale and the process effectiveness depended on the type and dose of surfactants used. Figure 9 shows that the investigated frothers can be classified into powerful and weak. The powerful frothers float well carbonaceous copper-bearing shale at a relatively low concentration (dose). For weak frothers the high recoveries are possible only at high concentrations.

Table 3. The average chemical composition of shales (based on [19, 20])

Components	Content, % mass
Cu	10.48
Ag	0.01
Pb	0.41
Ni	0.37
Mo	0.18
Co	0.04
Zn	0.078
Corg	8.04
SiO ₂	30.63
Al ₂ O ₃	10.01
CO ₂	9.90
CaO	7.94
MgO	4.05
Na ₂ O	0.32
K ₂ O	2.18
FeS ₂	0.66
FeO	0.49
Fe ₂ O ₃	1.01
S _S	2.64

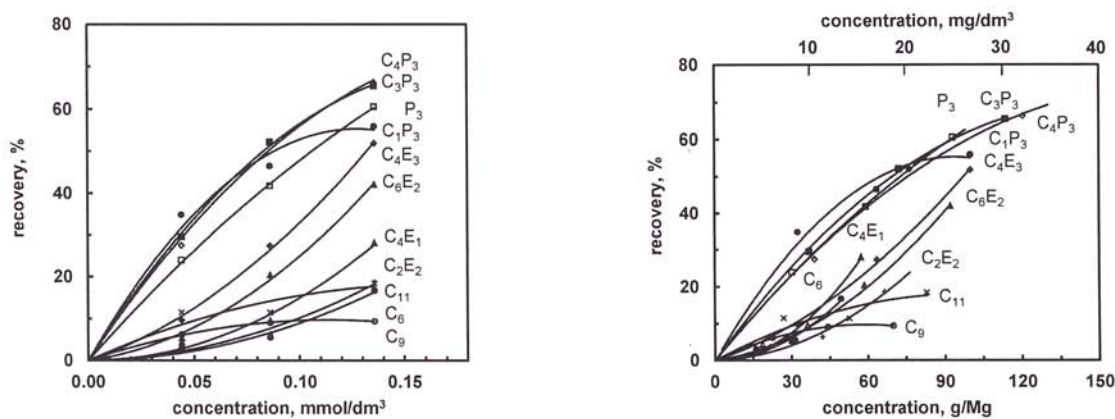


Fig. 9. Influence of frother concentration (dose) on recovery of shale [H7]

Figure 10 shows the influence of critical coalescence concentration (CCC_{95}) and number of carbon in alkyl group (C_n) of frother on the recovery of shale. Scattering of data is characteristic for random errors for CCC_{95} determination. As seen in Fig. 10, when the normalized concentration is

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presented in the form of ($c \cdot C_n / CCC_{95}$), frothers form one, somehow scattered family of lines, exhibiting almost the same behavior but at different concentrations.

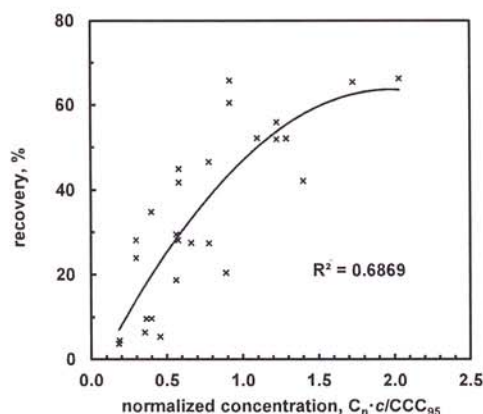


Fig. 10. Influence of normalized frother concentration (dose) on recovery of shale (based on [H7])

Although shale exhibits native hydrophobicity, with water contact angle greater than zero, it does not float in pure water. A lack of shale flotation and TPC formation in pure water does not result from its hydrophilicity but from stability of the interfacial water film separating the bubble and quartz surfaces. In pure water, both surfaces of shale ($pH_{iep} = 3$ [23]) and bubble ($pH_{iep} = 3$ [24]) are negatively charged and the repulsive electrostatic interactions prevent the film rupture, and therefore formation of a stable particle-bubble aggregate.

Moreover, the single bubble flotation tests conducted for shale with different degrees of roughness (Kowalczyk and Zawala, unpublished data) showed that there was no three-phase contact formation at the shale/liquid/gas interface in the presence of nonionic and cationic frothers. The addition of nonionic frother did not change the isoelectric point and surface charge of shale and bubble [23,24]. It is uncommon situation because on one hand shale floated with relatively high recoveries in both laboratory [H7, H8, H9] and industrial [25] scales, and on the other hand the three-phase contact was not formed. It suggests entrainment of shale. To check it I performed flotation of a model mixture of carbonaceous copper-bearing shale and quartz [H8]. Quartz is a convenient component of a feed since it does not float in the presence of short chain nonionic frothers. As seen in Figure 11, the addition of a nonionic frother improves flotation of shale, while low recoveries of quartz (less than 10%) are due its entrainment. It means that frothers do not change the real hydrophobicity of shale, but they “uncover” its effective hydrophobicity from zero up to the real, measured by the sessile drop technique, and make flotation possible [H9]. Figure 12 shows the influence of the frother dose on effective contact angle of shale. The effective contact angle was calculated by using a formula proposed by Varbanov et al. [26], which is based on the probabilistic model of flotation and the first-order kinetic equation.

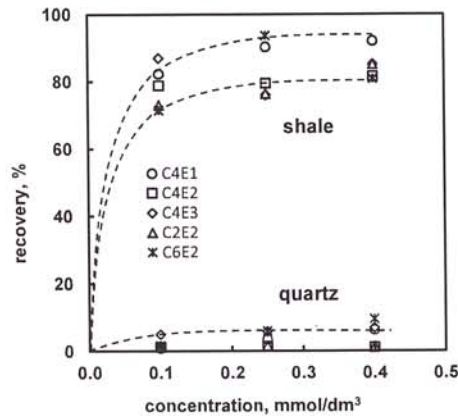


Fig. 11. Influence of frother concentration (dose) on recovery of shale and quartz [H8]

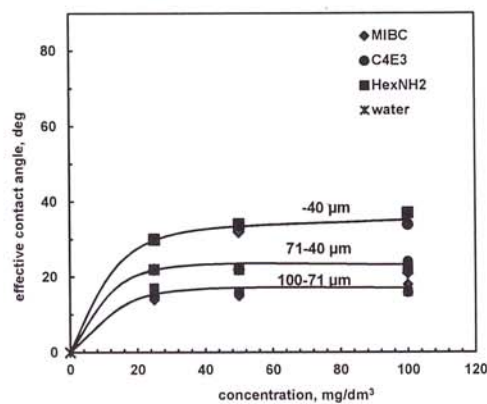


Fig. 12. Influence of frother type and concentration on effective contact angle of shale [H9]

Additionally, it can be assumed that flotation of carbonaceous copper-bearing shale in the presence of frothers only is not related with thinning the interfacial liquid film between bubble and solid surfaces and formation of three-phase contact but is due to the so-called contactless flotation, where the flotation response does not depend on the particle hydrophobicity and TPC formation [27]. The concept of contactless flotation was postulated by Derjaguin et al. [27]. In contactless flotation a particle-bubble aggregate is formed by the strong attractions at the secondary minimum of the DLVO theory without formation of mutual contact. The floating solids can be “fixed” at the liquid/gas interface and floated. More systematic studies are required to confirm the existence of this effect.

Flotation of highly hydrophobic polytetrafluoroethylene in water and in the presence of frothers

The previous paragraphs describe mechanism of flotation of slightly hydrophobic quartz as well as moderately hydrophobic fluorite and carbonaceous copper-bearing shale. In this paragraph I will present the results of flotation and single bubble tests of polytetrafluoroethylene, as an example of highly hydrophobic substance, in water and in the presence of frothers.

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Polytetrafluoroethylene (PTFE, Teflon®) is highly hydrophobic material with the water contact angle greater than 90° . It means that PTFE can be easily recovered by flotation in pure water without any surfactant (surface flotation). Indeed, flotation in water was very fast and after 5 sec all particles stayed at the liquid/gas interface. Figures 13 and 14 show that the flotation recovery and rate were strongly depended on the surfactant concentration. Higher concentration of frother decreased the flotation rate. Also the values of t_{TPC} fluctuated with the frother dosage (Figs. 14 and 15). The time of three-phase contact formation in water in at low concentrations of frother was very short and equal to 3.8 ms, whereas at higher concentrations was much longer and equal to 72 ms for $1 \cdot 10^{-3}$ M n-octanol.

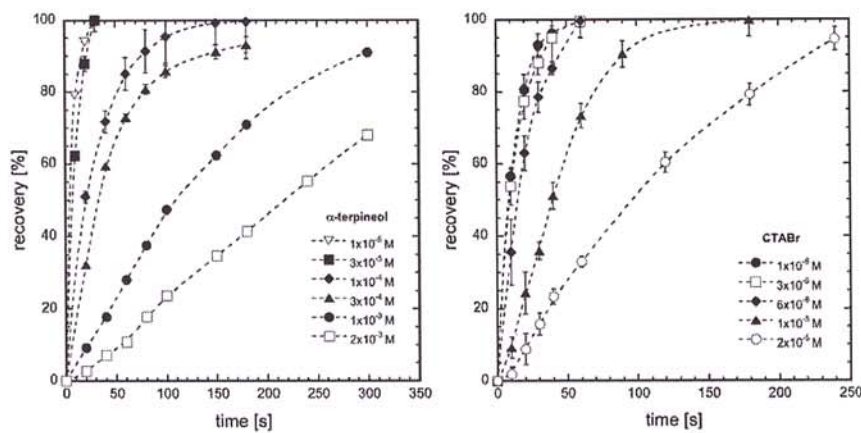


Fig. 13. Flotation recovery of polytetrafluoroethylene in the presence of frothers [H10]

Figure 14 shows that both flotation rate, expressed as an inversed values of the first order rate constant ($1/k$), and values of time of three-phase contact formation (t_{TPC}) varied in a similar manner, increasing equally within the same concentration range of frother (α -terpineol). This effect was observed for all the tested frothers [H10]. At very low frother concentrations a slight decrease in the t_{TPC} , in respect to distilled water, was observed. It was caused by the adsorption layer formation at the colliding bubble, for which the frother coverage was large enough for damping of the bubble bouncing [28] but insufficient for stabilization of the intervening liquid film formed between the bubble and hydrophobic Teflon surface (Fig. 16). However, at higher concentrations of frothers, the t_{TPC} values started to be prolonged due to the increasing stability of the liquid films formed by the colliding bubble. This prolongation was caused by the increased stability of the interfacial liquid film formed between the highly hydrophobic surface and colliding bubble. When the bubble collided with the solid having air entrapped at the surface, the foam films were locally formed. With increasing frother concentration the adsorption coverage at the liquid/gas interface increased, leading to a slower drainage and higher stability of the local foam films.

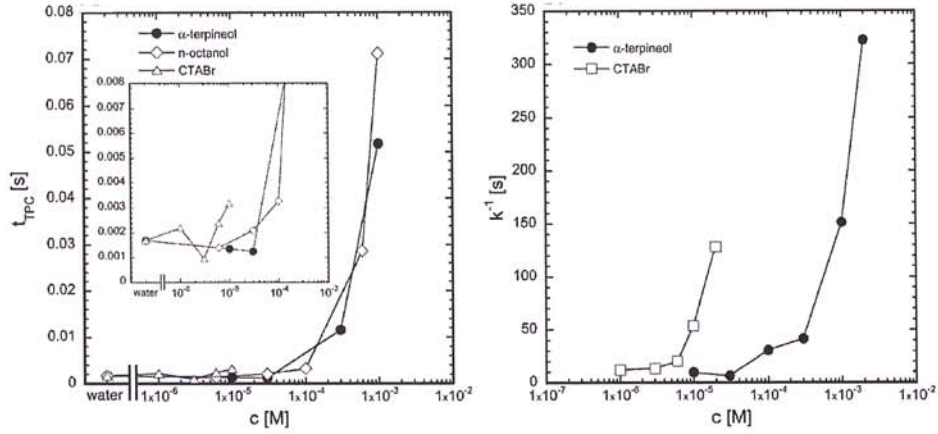


Fig. 14. Influence of frother dose on time of three-phase contact formation (left) and flotation kinetics (right) [H10]

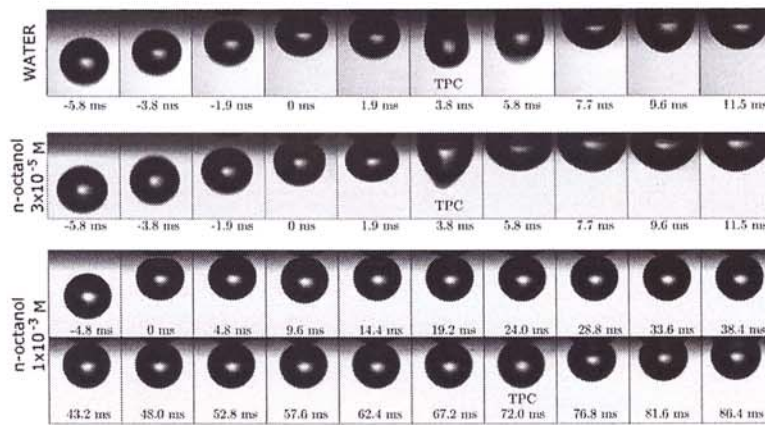


Fig. 15. Time of three-phase contact formation in water and in the presence of frother [H10]

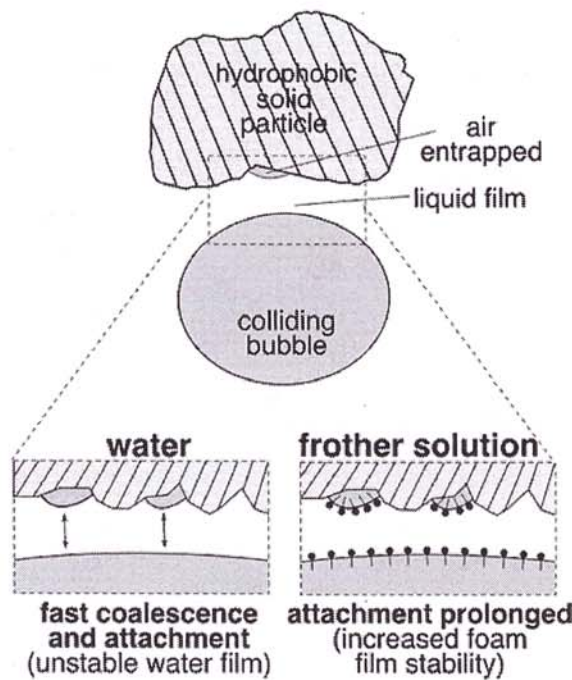


Fig. 16. Mechanism of bubble attachment to the PTFE surface in water and in the presence of frother [H10]

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Summary

In the autopresentation the results of my academic accomplishment were presented basing on a series of ten scientific publications combined into an essay on *Physicochemical aspects of flotation of naturally hydrophobic substances*. The most important achievements in the field of *mining and engineering geology* are:

- (i) derivation and presentation of the physical meaning of the Sauter mean diameter d_{32} used to express the average value of a collection of gas bubbles. The Sauter mean diameter of a set of spherical objects of different sizes is equal to the diameter of equisized spherical objects forming the collection. The polysized and equisized systems have different numbers of spherical objects, identical total surface area and identical total volume
- (ii) demonstration of a strong correlation between the critical coalescence concentration and ratio of hydrophilic-lipophilic balance to molecular weight. The proposed empirical model allows to predict the critical coalescence concentration from the chemical structure of frothers
- (iii) derivation of a new empirical model which allows to predict the Sauter mean bubble size d_{32} for any flotation frother
- (iv) calculation of surface energies and relaxation of surface ions for different planes of fluorite,
- (v) explanation of the mechanism of flotation of slightly hydrophobic quartz in water and in the presence of hexylamine as an example of short chain alkyl amine
- (vi) explanation of the flotation mechanism of naturally hydrophobic fluorite in water at different pH values
- (vii) explanation of the collectorless flotation mechanism of carbonaceous copper-bearing shale and better understanding the role of frothers in flotation of naturally hydrophobic solids
- (viii) explanation of the mechanism of worsening flotation of highly hydrophobic Teflon in the presence of frothers
- (ix) demonstration a strong correlation between time of three-phase contact formation and flotation kinetics expressed as the inversed first order rate constant k^{-1}
- (x) flotation kinetics is mainly determined by the time of three-phase contact formation, that is the time from the first bubble collision to its attachment to the solid surface. Despite the complexity of flotation process, which includes vast number of sub-processes, the kinetics of drainage of liquid film separating the bubble and solid surfaces seems to be a factor of a crucial importance for the final flotation outcome.

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5. Description of other scientific achievements

a) before Ph.D.

I studied at the Faculty of Fundamental Problems of Technology, Wrocław University of Technology in the field of materials engineering. In May 2008 under supervision of Dr. Tomasz Chmielewski I defended my M.Sc. thesis entitled *Chemical and mineralogical changes in non-oxidative and atmospheric leaching of copper ore shale fraction*, receiving a degree of master of science in chemical metallurgy and corrosion of metals. During my studies I started to work at the Wrocław University of Technology, first at the Faculty of Chemistry in the Group of Hydrometallurgy at the Department of Chemical Metallurgy, and then at the Department of Mineral and Waste Processing, Faculty of Geoengineering, Mining and Geology. In October 2008 I started my doctoral studies at the Faculty of Geoengineering, Mining and Geology. In May 2012 under supervision of Prof. Jan Drzymała I defended, with honors, my Ph.D. thesis entitled *Theoretical and*

experimental determination of the maximum size of flotation particles in different devices receiving a scientific degree of doctor of philosophy in mining and engineering geology with specialization of minerals engineering, materials engineering and physicochemistry of surfaces.

In the period of 2008-2012 I published 14 scientific papers, and 7 of them are included in the base of Journal Citation Reports (JCR).

Basing on the experimental and theoretical data, after their critical verification and application of my own innovative solutions, I showed that hydrodynamics of each flotation cell can be characterized by an empirical apparent cell constants, which characterize flotation dynamics and relate particle acceleration with advancing contact angle. As a result of my work I developed a flotation model which can be successfully used to predict the maximum size of floating particles based only on fundamental properties of a system such as dynamic cell constant, hydrophobicity and density of solids, surface tension of liquid and others. The results were published in: Kowalczyk, P.B., Sahbaz, O., Drzymala, J., *Maximum size of floating particles in different flotation cells*, Miner. Eng. 24(8), 2001, 766–771 (IF 1.352).

Knowledge on the maximum size of floating particles and empirical cell constants characterizing dynamics of flotation devices allowed one to determine the natural hydrophobicity of different substances expressed as the flotometric contact angle, which can be easily recalculated to the rest contact angle. The results were published in: Kowalczyk, P.B., Drzymala, J., 2011, *Contact angle of bubble with an immersed-in-water particle of different materials*, Ind. Eng. Chem. Res. 50(7), 4207–4211 (IF 2.237).

Basing on the crystallographic notation used to describe the structure of crystals and using a properly ordered letter and digital symbols a notation system was proposed which can be used to characterize any separation system. The proposed system is symbolic representation of separation procedure and the way of evaluation separation results is based on an easy-to-write sequence of signs helping a quick and precise understanding of the considered separation system. The proposed symbolism can be useful in applications such as computer programs and algorithms, fast communication and education on existence of other options of separation delineation. The results were published in: Kowalczyk P.B., Drzymala J., *A proposition of symbolism of non-ideal separations followed by analytical procedures for description of separation processes*, Miner. Process Extr. Metall. Rev. 32(4), 278–288 (IF 0.667).

In 2012 I published the *Letter to the Editor* in the International Journal of Mineral Processing (104-105, 80-81) when I found that another research group chaired by Dr. S.R. Grano worked on similar to my research topic but they did it improperly because to determine the maximum adhesive forces they used incorrect assumptions and formulas describing individual forces.



In 2008-2012 I participated in seven research and development projects realized at the Wrocław University of Technology. The most important projects were: BIOSHALE (*Search for a sustainable way of exploiting, black shale ores using biotechnologies*) within 6th Framework Programme; project Hydro *Hydrometallurgical technology for processing of copper concentrates and by-products* founded by National Centre of Research and Development within the IniTech program; and Ph.D. grant financed by National Science Centre.

In 2008-2012 I actively participated in 11 domestic and international scientific conferences and in 3 summer workshops for Ph.D. students organized by the Faculty of Chemistry, Gdansk University of Technology. In 2010 and 2011 I co-organized two Scientific Conferences for Ph.D. Students and Your Researchers, where in 2011 I was awarded for the best poster. In 2009-2012 I received the fellowship founded by the Rector of Wrocław University of Technology for the best Ph.D. students. In 2010 and 2011 I received two fellowships within the program of *Młoda Kadra* performed at the Wrocław University of Technology which was co-financed by the European Union within the European Social Fund. In 2011 I received the Rector of Wrocław University of Technology Award for scientific achievements.

In 2012 I spent six months at the University of Exeter, Camborne School of Mines working as a research assistant in the Prof. Hylke J. Glass group where I dealt with research and analysis of Near Infrared spectroscopy and Qemscan® of copper ores.

A full list of scientific publications and other achievements before Ph.D. is provided in Appendix 5.

b) after Ph.D.

The scientific research which I dealt with after Ph.D. was related to a number of activities that have a significant impact in the field of mining and engineering geology. My research work was related to four major aspects:

1) analyses of copper ore beneficiation results in the laboratory and industrial scales:

- i. development of the methodology for monitoring the copper ore beneficiation process in the industrial scale. The method is based on the statistical process control and detection of any changes which may lead to wrong decisions regarding the control of process. The results were published in: Tasdemir A., Kowalczyk P.B., 2014. Application of statistical process control for proper processing of the Fore-Sudetic Monocline copper ore. Physicochem. Probl. Miner. Process., 2014, 50(1), 247–262 (IF 0.926, MNiSW 25)*
- ii. conducting of a multivariate statistical analysis of basic upgrading parameters of copper ore from the Polkowice Division of Concentrators on the basis of industrial results obtained between 2011-2015. The proposed equation allows to predict the results of upgrading in*



total organic carbon basing on the data for copper and silver. The results were published in Duchnowska M., Kasińska-Pilut E., Bakalarz A., Konieczny A., Kowalczyk P.B., Łuszczkiewicz A., 2015. *Wielowymiarowa analiza statystyczna wyników wzbogacania rudy miedzi w ZWR Polkowice*. CUPRUM–Czasopismo Naukowo-Techniczne Górnictwa Rud, 2(75), 97–108

- iii. comparison and analysis of results of copper ore separation by means of flotation with frothers only (collectorless flotation). It was found that the best results were obtained by separation in the laboratory scale since the organic carbon-to-copper ratio was 2:1, while in the industrial scale this ratio was 1:1. These data indicated that the industrial pre-flotation concentrates should be subjected to a further treatment in order to lower the copper content and increase the content of organic carbon. The results were presented in: Konieczny A., Duchnowska M., Kaleta R., Pawlos W., Kowalczyk P.B., et al., 2015. *Analiza wyników usuwania węgla organicznego z rudy miedzi za pomocą flotacji spieniaczami*. XIth International Conference on Non-Ferrous Ore Processing ICNOP'2015, Trzebieszowice, 27-29.05.2015
- iv. analysis of kinetics of laboratory flotation tests of copper ore milling in the presence of three different grinding media (forged, high chrome and stainless). The flotation tests were performed at three different doses of industrial collector. The obtained results allowed to characterize the flotation kinetics of copper ore after milling under different conditions. The results were published in: Bakalarz A., Duchnowska M., Konieczny A., Kasińska-Pilut E., Pawlos W., Kaleta R., Kowalczyk P.B., Drzymała J., Łuszczkiewicz A., 2015. *Kinetyka laboratoryjnej flotacji rudy miedzi z ZWR Polkowice po mieleniu w obecności mielników o różnym składzie chemicznym*. CUPRUM–Czasopismo Naukowo-Techniczne Górnictwa Rud, 2(75), 55–70,

2) *application of near infrared spectroscopy (NIR) for analysis of copper ore:*

in collaboration with Camborne School of Mines, University of Exeter I published two scientific papers: i) Iyakwari S., Glass H., Kowalczyk P.B., 2013. *Potential for near infrared sensor-based sorting of hydrothermally-formed minerals*. J. Near Infrared Spectrosc., 21(3), 223–229 (IF 1.480, MNiSW 25); ii) Iyakwari S., Glass H.J., Rollinson G.K., Kowalczyk P.B., 2016. *Application of near infrared sensors to preconcentration of hydrothermally-formed copper ore*. Miner. Eng., 2016, 85, 148-167 (IF 1.597, MNiSW 35), in which I presented that near infrared sensors can be a very useful technique for the qualitative analysis of complex ores, and thus could be useful for the preconcentration of ores. This technique allows to reduce the costs of energy required for crushing and grinding the feed before the upgrading process.

3) investigation of properties of carbonaceous substances

- i. in two series of scientific monographs entitled *Łupek miedzionośny* (Carbonaceous copper-bearing shale) part 1 (2014) and part 2 (2016) edited by myself and Prof. Jan Drzymala the study of the influence of selected parameters such as type and dose of surfactants and pH on point of zero charge, hydrophobicity, flocculation, coagulation and flotation of carbonaceous copper-bearing shale originated from the Kupferschiefer deposit we published. The thermal analysis of shale was also presented.
- ii. presentation and discussion of the influence of the type and dose of frothers on contactless flotation of naturally hydrophobic hard coal. It was shown that the power (dose) of frother irrespective of the frother affected the maximum concentrate yield and upper particle size limit of floating particles. It was also shown that the selectivity evaluated basing on separation data, plotted as the recovery of the useful component in the concentrate versus the recovery of the remaining components in the tailing, decreased with increasing particle size. The highest selectivity was observed for fine particles, while the coarse particles were not beneficiated in a collectorless flotation of coal.

4) hydrometallurgical processing of copper ore:

during my research work I participated in the R&D project entitled *Hydrometallurgical technology for processing of copper concentrates and by-products* led by Dr. Tomasz Chmielewski from the Faculty of Chemistry, Wrocław University of Technology. The project was founded by National Centre of Research and Development within the IniTech program. The obtained results allowed one to develop of Polish Patent Application P405901 from 5. Nov. 2013 entitled *Method for the hydrometallurgical processing of polymetallic raw materials*.

A full list of scientific publications and other achievements after receiving the degree of Ph.D. is provided in Appendix 5.

6. Summary of scientific achievements

The summary of scientific achievements before and after receiving the Ph.D. degree as well as total Impact Factor, *h*-index and total number of citations are shown in Tables 4 and 5.

Table 4. Total number of citations and *h*-index

	Web of Science	Scopus	Google Scholar
total number of citations	61	60	123
Hirsch index (<i>h</i> -index)	5	4	6

Tabela 5. Summary of scientific achievements

	before PhD	after PhD	total
publications included in JCR	7	14	21
chapters in monographs and publications not included in JCR	2	19	21
papers published in conference proceedings	5	8	13
patent application	0	1	1
collective works	8	4	12
presentations at domestic and international conferences	9	19	28
participation in reserach projects	6	10	16
domestic and international awards for scientific activities	9	11	17
editor	0	4	4
total Impact Factor	8.648	18.425	27.073
total number of the MNiSW scores	188	373	561

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