Electrochemistry of Pyrite Flotation:
Second Maximum of Hydrophobicity

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On the potential dependencies of the various characteristics of pyrite hydrophobicity: detachment force, contact angle, gas evolution pressure and floatability we observed two maxima [1-3]. These results confirm data on the influence of potential on xanthate-induced floatability of pyrite [4]. W.J.Trahar mentioned that the reason for this behaviour is not known but the effect is well established. Whereupon it was suggested that the minimum is an artefact because the froth disappeared leaving apparently hydrophobic clusters of pyrite particles skin-floating on the surface of the pulp. However it could not be the reason of decreasing of pyrite hydrophobicity in [1-3] because those experiments were done without frother addition.

On the fresh non-oxidized surface of pyrite there are sulfur and iron sites with non-compensated negative and positive charges successively. These charges could be compensated both by regulation of pH or electrochemical potential. Measurements of electrokinetic potentials show that a total charge of pyrite surface is near zero in the origin of pH near 6. On the pH_{pzc} 6 the value of electrochemical potential is near +200 mV. This value could be considered as a potential of the point of zero charge or E_{pzc}. Stationary potentials values which are set up at pyrite are much more positive than the potentials of thermodynamic stability of the mineral.

Voltammograms of pyrite show that in acidic solutions pyrite surface is sulfur-covered, while in alkaline solutions it is covered with sulfur and Fe^{3+} hydroxide. These species determine the readiness for redox reactions and the hydrophobic and hydrophilic surface properties of the mineral. Under anodic polarization of pyrite in alkaline solutions starting from the stationary potential, it has been oxidized producing iron oxides and different forms of sulfoxide compounds. In electrochemical experiments, sulfur is oxidized to sulfate with large overpotentials. An anodic border of pyrite dissolution varies from 0.5 V in acidic to 0.2 V in alkali medium.

Evaluation of wettability and mechanism of bubble-mineral complex formation. There was studied a self-induced wettability and wettability, induced by xanthates with the different length of an alkyl chain. Study of pyrite wettability was carried out by contact angle, air bubble detachment force (ABDF), air bubble induction time (ABIT) air bubble evolution pressure (ABEP) and flotation experiments at various potentials of electrochemical polarization in buffer solutions with various pH. **ABIT** measurements show that the growth of the carbon chain of xanthate from ethyl to amyl resulted in decrease of an induction time and expanded an area of adhesion potentials. A process of bubble attachment to a planar surface is a rather slow one. ABIT experiments display only rough changes of mineral surface wettability and could be used only for the approximate comparison of it. **ABDF** measurements show that the detachment force/potential polarization curves are similar in shape for the case of xanthate absence and for all studied xanthates, Fig.1 [2].

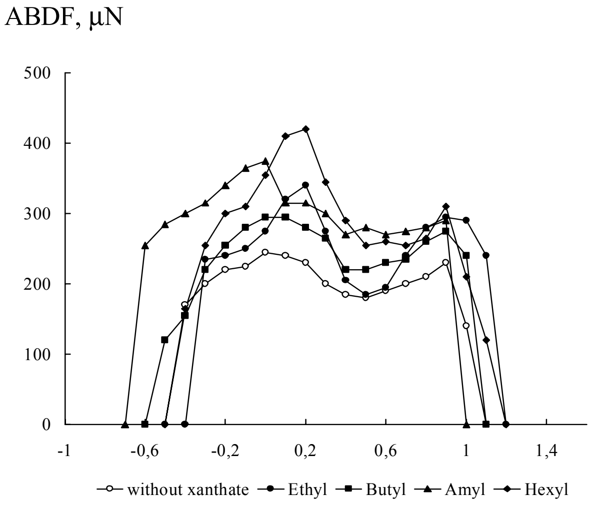

Fig.1. ABDF dependences on the potential of pyrite electrode

The curves exhibit two maxima and one minimum. With an increasing of an alkyl chain length the cathodic limit of an adhesion potential shifts to higher values. Potentials of the reduction between the maxima of the detachment forces are near 0.5V. If potential exceeds 0.16V dissolution of pyrite by stages is observed. After the first step pyrite surface is covered by hydrophilic iron hydroxide that leads to the increasing of resulting wettability. Qualitatively similar character of the dependences of hydrophobicity functions with and without collector leads to the conclusion that xanthate ions bloc iron sites that gives an input in total hydrophobicity, but the basic influence on it has a self-induced hydrophobicity of pyrite due to the S-sites.

The process of the formation of bubble-mineral particle complexes could be based on selective attaching of hydrophobic particles by air bubbles or on dissolved gas precipitation onto hydrophobic surfaces. Considering proposed mechanisms of froth flotation Arthur F.Taggart mentioned that “No appreciable part of the froth formed in the agitation-froth process is made by attachment of coursing air bubbles in the pulp to mineral particles therein, but substantially all air-mineral attachment is effected by precipitation of gas from solution onto sulphide surfaces” [5]. Numerous modern experimental results confirm this point of view. Under decompression on the mineral surface there are produced micro bubbles and preferably they will be appeared on the hydrophobic sites. Consequently surface wettability could be estimated by the comparison of the pressure decreasing that is enough for micro bubbles production. Comparison of Taggart’s evaluation of a suction behind blades of the impeller of an agitation-froth machine [5] and **ABEP** data on pyrite, Fig.2 [3], shows that gas evolution will be observed in the range of 1300-2700 revolutions of impeller per minute for hydrophobic and hydrophilic surfaces successively.

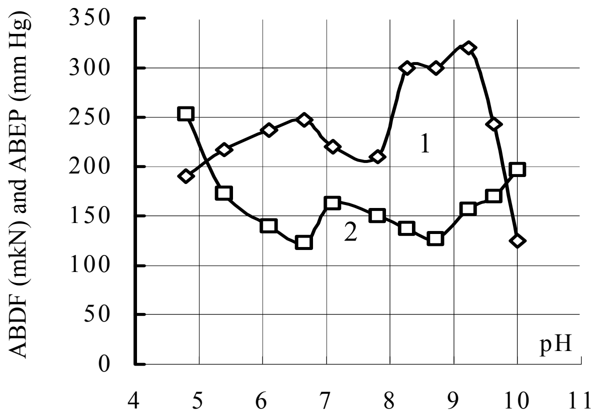

Fig.2. ABDF (1) and ABEP (2) dependences on the pH for pyrite

In first approximation ABEP-pH curve for pyrite is a mirror-like to the ABDF-pH curve, Fig.2. Structure of solid-liquid and liquid-gas borders has a determinative importance for formation of bubble-mineral complexes and subsequently flotation results. Water structure breaks near a hydrophobic surface facilitate water mass destruction and formation of gaseous phase embryos under decompression in an impeller zone. It simultaneously reduces a probability of produced micro bubbles dissolution as a result of pressure increasing owing to constant fluctuation of liquid densities into impeller zone.

Floatability-potential curves show that in the experiments with xanthate the both maxima are in the area of anodic potentials, Fig.3.

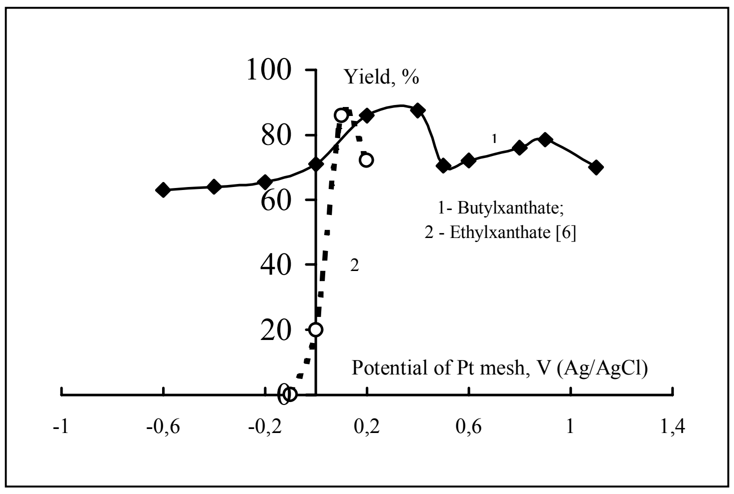

Fig.3. Pyrite floatability dependences on the potential of Pt mesh

The first maximum could be attributed with the processes of dixanthogen and elemental sulfur production. The probable reason for the second maximum of hydrophobicity and floatability of pyrite in strong oxidative conditions is a rapid elimination of the hydrophilic layer of iron hydroxide by a direct dissolution of mineral by reaction:

$$FeS_{2(s)} + 6h^+ + 8OH^- = 2S^o_{surf} + FeO_4^{2-} + 4H_2O$$

$$E = 0.45 – 0.08\ pH$$

Elemental sulfur production and subsequent process of gas evolution reduces kinetic limitations of the formation bubble-mineral complexes.

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