

¹G.A. Mun*, ¹D.Zh. Utkelov, ¹D.S. Kazybayeva,
¹A.O. Saduova, ¹R.A. Mangazbayeva, ²E. Negim

¹Al-Farabi Kazakh National University, Almaty, Kazakhstan

²University of Wolverhampton, Faculty of Science and Engineering,
 Wolverhampton, United Kingdom

*E-mail: mungrig@yandex.ru

Synthesis and study of phosphate-polyalkyleneoxide flotation reagent for oxidized minerals

Abstract. Polyalkylene oxidephosphates were obtained by phosphorylation of polyethylene oxide and polypropyleneoxide of different molecular weight. Evaluation of flotation activity in experiments on the extraction of tungsten oxide from wolframite pulp showed that the introduction of oxygen donor atoms into phosphate group substituent, responsible for hydrophobization of the surface of mineral particles, increase the degree of the heavy metal extraction.

Key words: polyalkylene oxidephosphates, flotation, extraction, oxidized.

Introduction

Progress in the field of ore enrichment is largely determined by flotation reagents. Use of more efficient compounds from their number provides a greater, compared to their value, economic benefit. Because it allows extracting metals from ores without significant additional capital costs and to lower operating costs. Problems in refining and metallurgical processing are low concentration of valuable components in ores and rock strength though the total content of minerals in the Republic may be large, on the whole. Due to processing of raw materials with complex composition and often poor ores, as well as appearance in the chemical industry sector of new resources and goals, particularly, in the energy efficiency and environmental standards sector, involving in the production process of effective flotation reagents is particularly important. Almost all flotation reagents used by Kazakh processing enterprises are imported products. Therefore, the State Program on Forced Industrial-Innovative Development of Kazakhstan for 2010 – 2014 years, envisages organizing of production of new types of chemical products, including flotation reagents in Kazakhstan [1-3].

In present paper the ways to obtain competitive flotation reagents by evaluating the impact of the hydrophobic part of their molecules on the degree of con-

centration of the oxidized minerals flotation were determined. The flotation reagents with the same ionic groups but different in size were synthesized and structure of their hydrophobic substituents and their flotation performance were compared.

Materials and methods

Materials

Polyethylene glycol (PEG) of molecular weight (Mw) of 450, 500, 600, 1000. Polypropylene glycol (PPG) Mw 250, 540, 600, 1000, 4500. Aliphatic alcohols fractions C₈ Mw 96 C₁₀ Mw 120 C₇₋₂₀ Mw 84-240, C₃₀₋₃₃ Mw 360-396. Ether, phosphorus pentoxide, phosphorus oxychloride – products available commercially.

Synthesis of flotation reagents

Synthesis of flotation reagents by reacting alcohols with phosphoric anhydride and with phosphorus oxychloride.

a) Preparation of alkylphosphates by reaction of various alcohols with phosphorus pentoxide. 14 g (1 mol) of P₂O₅ (dry fine powder) were added to a 0.5 M of an alcohol with vigorous stirring, and reacted at a temperature of 90° C until complete dissolution of all P₂O₅ during 6 hours.

b) Preparation of alkylphosphates by reaction of various alcohols with phosphorus oxychloride. 3.03

g (0.03 mol) of triethylamine (TEA) and 0.03 mol of alcohol in 50 ml ether for 1.5 h was added to a mixture of 250 ml of ether and 4.70 g of POCl_3 (0.03 M) with vigorous stirring and cooling (00C). The reaction mixture was kept under stirring and further cooling for 6 hr., the precipitated salt was filtered off, washed thoroughly with ether. The solvent was distilled off on a water bath. The product was dried in a vacuum oven.

Characterization of flotoreagents

The resulting compounds of alcohols phosphorylation were identified by IR spectroscopy.

Performance was evaluated by the degree of extraction of tungsten oxide from minerals scheelite and wolframite.

Minerals flotation was carried in the flotation machine of 50 ml volume. For the experiment, samples of 3 grams of mineral with grinding fineness 140 +/- 50 microns were used. Flotoreagents were prepared as the aqueous solutions with a concentration of 0.05% by weight of the mineral. Flotation was carried out in distilled water in the flotation machine at a pH of 6.5-7.5. Flotation time was 3 min.

Results and discussion

Flotation reagents were prepared by known-phosphorylation reaction of alcohols with pentoxide and with phosphorus oxychloride.

Proposed structure of the synthesized flotoreagents was confirmed by IR spectroscopy. A set of bands in the IR spectrum in the region of 2700-2450 cm^{-1} corresponds to the valence vibrations of associated OH groups- $\text{PO}(\text{OH})_2$, the valence vibrations of $\text{P}=\text{O}$ correspond to a weak band 1240 cm^{-1} . Intense peak of 1045 cm^{-1} is related to the presence of the C-O-P, a band of 1170 cm^{-1} indicates the relationship of the branched alkyl substituent Alk-C-O-P . A small amount of P-Cl bonds are appointed by the weak band 580 cm^{-1} .

The resulting compounds were evaluated for flotation extraction activity of tungsten trioxide minerals scheelite and wolframite. Experiments in the case of the reaction of alcohols with phosphorus pentoxide revealed that the greatest degree of extraction of tungsten have collectors obtained at 80°C, with the ratio of alcohol: P_2O_5 equal in moles of 1:2, during 6 hours. Products obtained under these conditions were able to extract up to 65% tungsten oxide (table 1).

Significant improvement of the collecting properties of the obtained alkyl phosphates has been

achieved in the preparation thereof by reacting alcohols with phosphorus oxychloride. Experiments to select optimum conditions for the reaction of alcohols with POCl_3 were conducted using the alcohols, which showed the best results in the alcohols' reaction with P_2O_5 : from paraffin- C_{30-33} alcohol, polyethylene glycol (PEG) - having a molecular weight of 4500, from polypropyleneglycol (PPG) - having a molecular weight of 4500 and, for comparison with a molecular weight of 250.

Table 1 – Flotation activity of the reagents obtained by reaction of alcohols with phosphorus pentoxide (alcohol: P_2O_5 =1: 2mol;90°C; 8 hours)

Alcohols	Molecular weight	Degree of extraction WO_3 , %
C_8	95	18
C_{10}	120	18
C_{7-20}	84-240	20
C_{30-33}	360-396	20-21
Polyethylene glycol	450	23
	500	37
	600	46
	1000	52
Polypropylene glycol	250	33
	540	49
	600	51
	1000	60
	4500	65

The above data in table 1 of flotation activity of the phosphate obtained by alcohols treatment with phosphorus pentoxide indicate that phosphor-ester group together with the oxygen donor atoms of the hydrophobic moiety »work» more effectively. Enlargement of the paraffin substituent at the phosphor-ester group does not increase the degree of extraction of tungsten. Increasing the aliphatic length from C_8 to C_{30-33} virtually has no effect on flotation. The introduction of the oxygen atoms having high affinity for tungsten atoms into the paraffin chain appreciably increases the degree of oxidized mineral extraction.

Experiments carried out in the same manner have shown that in the case of phosphorylation of alcohols by phosphorus oxychloride, flotation activity depends essentially on the nonionic moiety of a reagent. Increasing the size of the oxyalkylene substituent at the phosphate group increases the efficiency of the collector (Table 2). Varying the ratio

of reactants (0.2-2.0 moles of POCl_3 per mole of alcohol) showed that the most suitable in the event of a collector on the basis of PPG with molecular weight 4500 is an equimolar ratio.

Table 2 – Flotation activity of the reagents obtained by reacting alcohols with phosphorus oxychloride (alcohol: POCl_3 = 1: 1 in moles; 0°C, 8 hours)

Alcohols	Molecular weight	Degree of WO_3 extraction, %
Paraffin fraction C_{30-33}	360-396	21
Polyethylene glycol	450 1000	22 49
Polypropylene glycol	250 4500	35 89

Products of alcohols phosphorylation by phosphorus oxychloride are significantly different from each other. A phosphoric ester group with simple aliphatic chain C_{30-33} «works» at around 20%, and together with the donor atoms of oxygen in the hydrophobic chain acts much more effectively: with polyethylene oxide groups at up to 49%, and with polypropylene oxide groups obtained flotation reagent extracts up to 89% WO_3 .

The results of the experiments shown in Tables 1 and 2 suggest the following conclusions:

- the sizes of the molecule of the initial alcohol, and accordingly, the alkyl substituent on the phosphate group, significantly affect the efficiency of flotation;

- the size of paraffinic substituents affect on the collective properties of the products much weaker than in the case of hydroxyalkyl substituents;

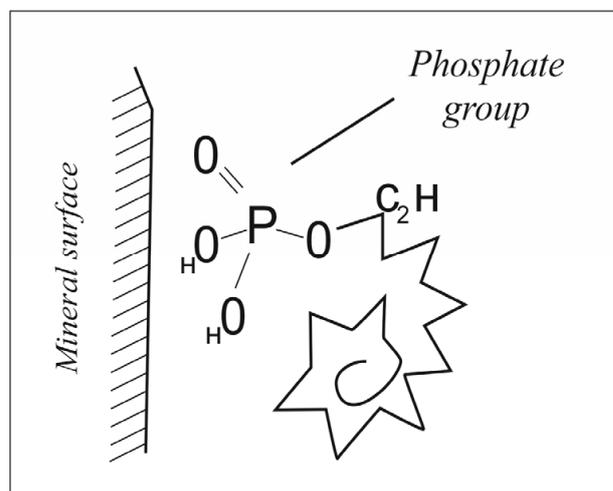
- considerably higher flotation ability of the alkylene oxide reactants in comparison with collectors based on paraffinic alcohols is obviously caused by chelating with the surface of minerals not only by the ionic phosphate group, but the ether oxygen atoms of hydrophobic moieties as well;

- polypropylene oxide substituent is more efficient than the polyethylene oxide one.

The literature on the mechanism of interaction of the ore particles with flotation reagents, separated forces that cause adsorption, as physical and chemical. It is considered that the selective interaction provides chemisorption. Realization of chemical bonds through donor-acceptor interaction makes possible

to distinguish between heavy metal ions extracted and waste rock particles. Ionic hydrophilic portion of flotation reagent's molecule is serving as a donor and atoms of heavy metals with unfilled d-orbitals as an acceptor. Thus, it is generally accepted that the chemical bonding of anionic groups of a collector with mineral cation (or, respectively, cationic collector with mineral anion) leads to the introduction of reagent hydrophobic parts into a zone of hydrate-layer, weakening and destruction of the latter, and to the formation of the layer of the hydrocarbon chains on the particle surface, which are able to cling to the air bubble [4-13].

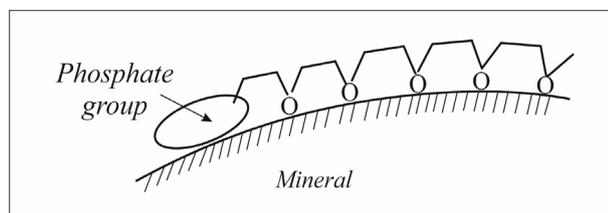
In the case of phosphate reagents synthesized in the present work a big difference in the activity of collectors with alkyl and oxyalkyl substituents may be due only to the fact that the latter are involved in the formation of bonds with tungsten ions. Moderate effect of increasing length of the hydrophobic substituent of the phosphate group on the activity of the flotation reagents based on paraffinic alcohols obviously due to the following. Fatty polymethylene chain of alkylphosphate trying to reduce its volume in water, should curl up into balls. Hydrophobized mineral part of a particle surface is only the surface of the coils.



Increasing the length of the chain (in this case from C_8 to C_{33}) slightly increases the surface rolled-coils. Accordingly, it slightly increases the degree of water-repellency and extraction of WO_3 - from 18% to 21% of C_8 to C_{33} .

Significantly greater effect should be in the case when the hydrophobic coils are deployed in chain stretched along the surface of mineral. This is

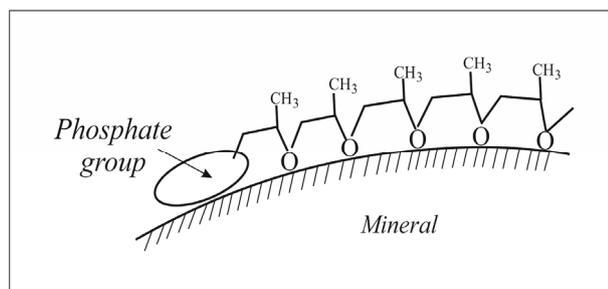
achieved by the introduction into alkyl substituents of the donor atoms of oxygen interacting with the atoms of the heavy metal tungsten on the surface of the mineral particles.



Increasing the length of the ethylene oxide chains increases the hydrophobized surface of mineral particles, and thus the degree of extraction of tungsten oxide. In our case from 22-23% for polyethylene glycol with a molecular weight of 450 up to 52 and 49% for the polyethylene glycol with a molecular weight of 1000 (Table 1 and 2).

A further increase of the degree of extraction – up to 89% – is achieved in the case of polypropylene oxide chains.

Additional methyl groups double the thickness of the hydrophobic layer, substantially increase the likelihood of exposure of the hydrophobized spots with air bubbles:



Conclusions

Ideas about strong enough adhesive interaction of the functional groups and the donor atoms of the hydrophobic part of the flotation reactant molecules to the surfaces of the ore particles were useful not only for understanding the mechanism of a possible increase in the selectivity of the flotation, but were purposefully used in the synthesis of flotation re-

agents with high flotation degree of wolframite. It was achieved by introducing oxygen donor atoms into the hydrophobic part of the collector molecules.

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