Peculiarities of the DC-80 reagent based on acetylenic alcohols effect in flotation processes

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T. I. Yushina, *Professor, Acting Head of Mineral and Waste Material Processing and Treatment Department*[1], *e-mail: yuti62@mail.ru*
O. A. Malyshev, *Director General*[2]
S. A. Shchelkunov, *Technical director*[2]
D. P. Khrustalev, *Assistant Professor, Department of pharmaceutical disciplines with chemistry course*[3]

[1] *The National University of Science and Technology "MISiS", Moscow, Russia.*
[2] *Innovation Resource Ltd., Moscow, Russia.*
[3] *Karaganda State Medical University, Karaganda, Kazakhstan.*

The paper is devoted to analysis and examination of DC-80 (ДК-80) nonionic surface-active reagent based on acetylene alcohols aberrant behaviour mechanism during flotation of non-ferrous metal ores, coking coals and carbon nanomaterials.
Presented are results of the properties and flotation behaviour comparison for DMIPEC (ДМИПЭК) and DC-80 allied reagents based on acetylenic alcohols.
The DMIPEC and DC-80 reagents are obtained by interaction of acetylene and acetone. The main matter in DMIPEC reagent has a conjugated π-electrons system, consisting of a combination of acetylene and ethylene bonds, and DC-80 molecule possesses single acetylene bond. Acetylene bond is prone to selective interaction with cations of non-ferrous and noble metals. In the view of the authors, the DC-80 reagent being a surface-active substance by diphilic molecule structure and possessing high aqueous solubility due to hydrophilic and lipophilic balance, doesn't reveal any surface activity and hence it can be absorbed as an additional collector by means of π-complexes formation on the surface of sulphides and a frother should be required for the flotation realization. However, practice of flotation has shown the effect identity of DC-80 and DMIPEC reagents.
It is shown in the paper that acetylene-based reagents demonstrate properties of selective surface hydrophobization of sulphide minerals and carbonic materials and at the same time gain foaming capability. At that, selectivity and speed of flotation, quality of concentrates, increase of flotation capacity and efficiency, reduction of material capacity are provided.

Key words: flotation, frothers, collectors, acetylenic alcohols, cations of non-ferrous metals, coal, nanocarbonic materials.

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Modern state of the world market of metals, minerals and chemical products is determined on the one hand, by continuous growth of amount and quality of products under conditions of increasing wild-life conservation requirements and multipurpose utilization of raw materials and on the other hand, by deterioration of the mind minerals processing characteristics. In order to support and increase the production facilities of enterprises of mining and smelting and ore mining and processing industry, base and difficult for concentration ores are more and more being involved into processing along with man-caused and non-commercial raw materials [1, 2].

In conditions of steady declining quality of raw materials, an amount of valuable components extracted from a ton of processed ore is a dominating factor. Optimization of material resources consumption per ton of processed ore and increase in labour productivity are of no small importance for solving this problem. Expansion of an intellectual component in the mineral raw material enrichment process is a key factor for profitable functioning of the Russian metal mining industry in conditions of world competition.

Recently, the main concentrating process for various types of minerals is flotation as before. Different lines of its perfection are known: development of new reagent practices and optimization of the existing ones; creation of new high-performance equipment; application of the enrichment processes computerized testing; magnetic, magnetic electropulse and electrochemical working of flotation systems etc. [2–5].

The object of our investigations is a search of new approaches to the rate, completeness and selectivity of the minerals extraction increase using double-acting flotation agents with acetylenic bond.

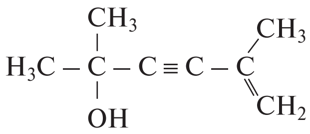
Studied are the flotation properties of DMIPEC and DC-80 reagents on flotation of different types of mineral – copper, gold-bearing copper-zinc, copper-nickel ores, coking coals and nanocarbonic materials [6, 7].

It is found that the DMIPEC reagent usage allows to increase the valuable components extraction by 1.5–12.0% along with the concentrates quality and flotation rate improvement [6]. In the author's opinion, efficiency of reagent is connected with demonstration of additional collecting properties stipulated by selective DMIPEC adsorption on minerals of non-ferrous metals, the surface of which is in a hydrophobic state and consequently is inaccessible for ionogenic sulfur-bearing principal collectors [6].

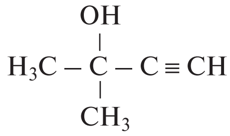
Flotation reagent dimethyl(isopropenilethynyl)carbinol (DMIPEC) $(CH_3)_2C(OH) - C \equiv C - C(CH_3) = CH_2$ is an additional collector with foaming properties. It is produced by direct interaction of acetylene and acetone with subsequent dehumidification of the reaction product at the stage of its purification by rectification [6, 8].

Flotation reagent DC-80 $(CH_3)_2C(OH) - C \equiv CH$ is also a light-yellow liquid with a faint hydrocarbon odor; it is non-toxic. Structurally, it is an individual compound obtained by direct interaction of acetylene and acetone, followed by monodehumidification of the reaction product.

Structural formulas of the reagents are as follows:



DMIPEC reagent

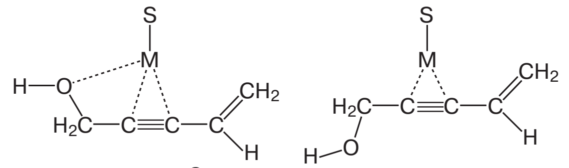


DC-80 reagent

It is known that acetylene bond is prone to selective interaction with cations of non-ferrous and noble metals [9]. The main matter in a DMIPEC reagent has a conjugated π-electrons system consisting of a combination of acetylene and ethylene bonds, and is a typical surface-active substance.

Since the DMIPEC reagent synthesis process of acetylene and acetone with subsequent monodehumidification and regeneration of alkaline catalyst in stoichiometric quantities is a two-stage and relatively laborious, it has been decided to study a DC-80 flotation reagent in the flotation of sulphide ores of non-ferrous metals. This reagent is a one-stage received of the same substances but in other proportions; moreover, the required amount of catalyst is 100 times less [10].

Forecast of the prediscovery successfulness has been founded on the fact that according to the electronic theory of organic chemistry [11], interaction of common π-electrons of the DMIPEC reagent ethylene and acetylene bonds with cations of non-ferrous metals is much more stronger than that of the DC-80 reagent, a base material of which is dimethyl(ethynyl)carbinol containing an acetylene bond only (Fig. 1). That's why an anxiety has existed that single acetylene bond would not be enough to achieve the successful flotation results. Besides, the DC-80 reagent being a surface-active substance by diphilic molecule structure, which contains polar (hydrophilic) and apolar (hydrophobic) parts and possesses high aqueous solubility due to hydrophilic and lipophilic balance doesn't reveal any surface activity. Hence, this reagent can be absorbed as an additional collector by means of π-complexes formation on the surface of sulphide minerals (Fig. 1), and a frother should be complementary required for the flotation realization.



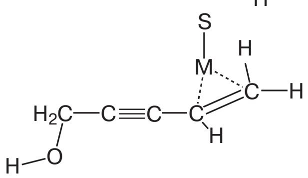


Fig. 1. Structural formula of a pentene-1-in-3-ola-5 model molecule and sulphides of non-ferrous metals MS interaction results

Choice of an optimum frother allows to significantly increase selectivity and results of flotation, since flotation rate, cleaner processes and solid particles circulation in a foam layer are to a marked extent determined by its properties [3, 12, 13]. In practice, this is as a rule achieved by simultaneous application of different frothers [3]. Currently, the non-ionogenic oxygen-containing compounds or alcohols are the most widely used [13].

Capability for direct frother interaction with mineral surface is typical for the compounds containing double $- C = C -$, $C = O$ bonds. It is known that frothers action selectivity on ores flotation may be increased by introducing to their structure some specific complexing groups. Thus, introducing an acetylene or polyglycol group into a molecule of surface-active substance stipulates its preferable absorption on the surface of copper and silver minerals [9]. Applying frothers with adjustable collecting capacity allows to significantly reduce losses of noble metals during flotation of sulphide gold-bearing ores [3, 9]. Some frothers can directly interact with the surfaces of certain minerals thus increasing a degree of their hydrophoby and selectivity of flotation by means of orientation, inductive and hydrogen bonds as well as disperse forces resulting in change of composition and share of physically sorbed molecules in adsorption layer of the collector [13]. Influence of molecules of the frother and other hydrophobic apolar and heteropolar organic matters on minerals floatability is stipulated not only by changing the hydrophoby degree and correlation of the sorption forms on the surface, but also by modifying the bubble of air or gas surface relaxation characteristics during a mineral particle attaching on it [3, 14, 15].

Results of DMIPEC and DC-80 reagents flotation investigations implemented on different types of non-ferrous and noble metals have showed that direct interaction of these reagents with cations of certain metals of certain minerals results in increase of their hydrophoby and flotation selectivity rates. In that way, the frother action selectivity during flotation of minerals is determined by correspondence of steric and electronic parameters of mineral surface and the "collector-frother" complex formed on it [13].

Efficiency of DMIPEC and DC-80 reagents has been also demonstrated during the coking coals and carbon nanomaterials flotation [6]. In that case, DC-80 reveals itself as a frothing agent with collective properties. The reagent consumption has amounted to: for coal — 50–100 g/t (in case of joint use with apolar collector), 120–500 g/t (on individual use); for carbon nanotubes (CNT) separation from ferrimanganese composite — 120–150 g/t. An additional combustible mass extraction to foam product has made up 3–8% at essential increase of the flotation waste ash content, while a natural hydrophobic CNT recovery into foam product has been equal to 85–96% depending on reagent consumption. At this, the best results on the flotation CNT recovery have been obtained with the use of DC-80 as compared to DMIPEC and $C_7 - C_{12}$ aliphatic alcohols (Fig. 2). In case of CNT flotation, DC-80 has acted as a collector-frother.

Test laboratory experiments implemented on copper-zinc ore of the Dzhidinsk deposit have showed (Table 1), that interaction of DC-80 with copper and zinc cations is strong enough and its usage in combination with T-80 provides an advanced yield (by 12.3 and 4.0% of copper and zinc, respectively) in a rough flotation with significant selectivity decrease in comparison with reference experiment. Concentration degree lessens from 3.97 to 2.7% of copper and from 2.92 to 1.75% of zinc. However, it has been noted that selectivity is paradoxically increased on adding an extra amount of DC-80 to T-80.

Table 1
Results of rough flotation of the copper-zinc ore of the Dzhidinsk deposit

Name	Yeild, %	Content, %		Recovery, %		Conditions of experiment
		Cu	Zn	Cu	Zn	
First series of experiments						
Rough flotation concentrate	11.56	4.25	3.39	45.70	33.74	T-80 20 g/t
Rough flotation tailings	88.44	0.66	0.87	54.30	66.26	
Ore	100.00	1.07	1.16	100.00	100.00	
Rough flotation concentrate	15.81	3.28	2.15	41.45	23.29	T-80 20 g/t + + DC-80 5 g/t
Rough flotation tailings	84.19	0.87	1.33	58.55	76.71	
Ore	100.00	1.25	1.46	100.00	100.00	
Rough flotation concentrate	21.44	3.49	2.57	58.00	37.74	T-80 20 g/t + + DC-80 10 g/t
Rough flotation tailings	78.56	0.69	1.17	42.00	62.51	
Ore	100.00	1.29	1.47	100.00	100.00	
Second series of experiments						
Rough flotation concentrate	12.92	5.85	3.94	40.22	22.36	T-80 20 g/t
Rough flotation tailings	87.08	1.29	2.03	59.78	77.64	
Ore	100.00	1.88	2.28	100.00	100.00	
Rough flotation concentrate	12.23	5.47	4.18	41.55	24.76	DC-80 10 g/t
Rough flotation tailings	87.77	1.09	1.77	58.85	75.24	
Ore	100.00	1.63	2.06	100.00	100.00	
Rough flotation concentrate	16.07	6.01	4.22	55.85	33.42	DC-80 15 g/t
Rough flotation tailings	83.93	0.91	1.61	44.15	66.58	
Ore	100.00	1.73	2.03	100.00	100.00	

Table 2
Results of flotation of copper-zinc ores of the Akbastau deposit

Name	Yeild, %	Content, %		Recovery, %		Conditions of experiment
		Cu	Zn	Cu	Zn	
Cu head	3.15	19.80	4.25	31.09	16.20	Res. CaO in reused water 250 mg/l; class –0.074 mm — 75%; To head: Na_2S = 70 g/t; *Kx* = 20 g/t; DMIPEC = 5 g/t; to rough flotation: *Kx* = 190 (50+140) g/t; $ZnSO_4$ = 150 g/t; DMIPEC = 5 g/t; Control flotation: *Kx* = 100 g/t
Rough flotation concentrate	24.10	5.27	2.61	63.37	76.19	
Middlings of final recleaner flotation	7.95	0.58	0.22	2.30	2.12	
Tailings	64.80	0.10	0.07	3.23	5.49	
Ore	100.00	2.00	0.83	100.00	100.00	
Cu head	3.34	21.34	4.41	36.01	17.91	The same, but with the use of DC-80 instead of DMIPEC
Rough flotation concentrate	27.40	4.28	2.25	59.29	75.02	
Middlings of final recleaner flotation	6.40	0.57	0.22	1.85	1.71	
Tailings	62.86	0.09	0.07	2.86	5.35	
Ore	100.00	1.98	0.82	100.00	100.00	

Analysis of this fact has lead to the conclusion that deterioration of selectivity characteristics is caused by an excessive amount of T-80 frother. Addition to the principal collector the DC-80 only has allowed to improve results of reference experiments on both selectivity and copper and zinc recovery to concentrate (by 15.63 and 11.07%, respectively). Concentration degree has increased from 3.11 to 3.47% of copper and from 1.72 to 2.08% of zinc, as compared to the standard.

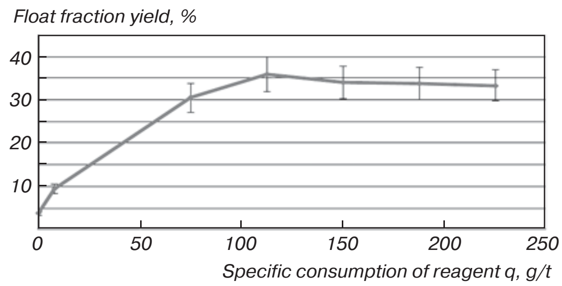


Fig. 2. Graphic chart of floated fractional yield (%) dependence on the DC-80 reagent consumption (g per ton of composite)

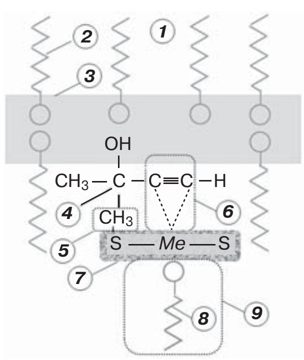


Fig. 3. Shematic sketch of the form of mineral particles attaching on a foam bubble in DC-80 presence:
1 — air inside the bubble; *2* — frother; *3* — bubble envelope; *4* — molecule of a DC-80 supplementary collector-frother; *5* — zone of van der Waals intercation; *6* — zone of π-complex formaiton; *7* — surface of a sulphide mineral colloid small part; *8* — sulfur-bearing collector; *9* — hydrophobizated zone of a mineral

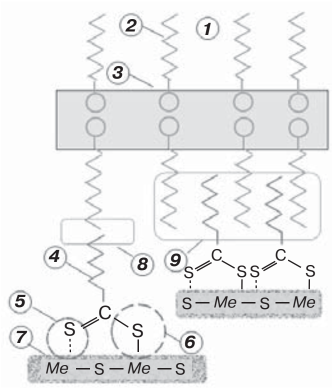


Fig. 4. Shematic sketch of the form of mineral particles attaching on a foam bubble in potassium butyl xanthogenat (PBX) presence:
1 – air inside the bubble; *2* — frother; *3* — bubble envelope; *4* — molecule of collector (PBX); *5* — zone of van der Waals intercation; *6* — zone of a covalent bond formaiton; *7* — sulphide mineral surface; *8* — zone of van der Waals intercation; *9* — hydrogen bond

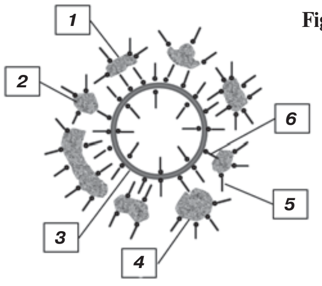


Fig. 5. Shematic sketch of a bubble mineralization in presence of DC-80 molecules:
1 — contact with the bubble through the hydrophilic zone of a mineral; *2* — contact with the bubble through the hydrophobizated zone of a mineral; *3* — bubble; *4* — sulphide mineral; *5* — principal collector (PBX); *6* — DC-80 reagent

Experimental conditions: ore has been grinded up to coarseness of 90% class – 0.074 mm. Feeded to grinding was $Na_2S{\cdot}9H_2O$ — 30 g/t. Consumption of CaO — 7 kg/t, potassium butyl xanthogenate (*Kx*) — 30 g/t, amount of frother has varyed, feeding density — 30%, time of rough flotation — 10 min.

Test experiments implemented on copper-zinc ore of the Akbastau deposit (Table 2) have confirmed the action identity of DC-80 reagent without surface activity and DMIPEC reagent which is a nonionic surface-active substance with foaming properties.

In our opinion, foaming capacity of DC-80 is proved due to its hydrophobic piece lengthening because of the part of acetylene bonds absorption on the surface of colloid particles of sulphide ore minerals, which contain cations of non-ferrous metals situated in hydrophobic environment formed by molecules of sulfur-bearing collecting agents (Fig. 3).

The authors suppose that molecules of DC-80 reagent fixed on the surface of sulphide minerals colloid particles may simultaneously be a structure of an envelope of air-bladders through lyophilic group OH. In such a form the DC-80 reagent molecules evince properties of supplementary collectors and can simultaneously take part in formation of foam bubbles by generating an organo-mineral complex and thus demonstrating foaming behaviour not typical for individual molecules of DC-80 reagent.

It is necessary to point out that organic surface-active substances provide increase of the extracted minerals flotation features not only due to the surface hydrophobization but to the formation of surface-active organo-mineral complexes as well.

Analysis of the shematic sketch of the form of mineral particles attaching on an air bubble with traditional collectors and frothers (Fig. 4) has showed a distinct difference in a structure of their attaching on the mineral particle and an envelope of the bubble.

Complex of anomalous features of the DC-80 reagent molecules becomes apparent in the fact that structurally being a surface-active substances which don't form a foam in the water [12], they are able to form the selective complex compounds with surfaces of sulphide minerals and thus allowed the obtained organo-mineral complexes to reveal foaming capacity and provide such a physical process as flotation (Fig. 5). In our opinion, the process of a bubble mineralization during flotation of natural hwydrophobic materials such as coking coals and carbon nanotubes will look in much the same manner.

Experiments on flotation of the Akbastau ore of a narrow size grade have showed that in case of absence of colloid particles less than 45 μm and more coarse +75 μm, the copper and zinc recovery is sharply decreased but flotation activity of minerals is restoring as consumption of the standard frother grows (Table 3).

Table 3

Results of flotation of copper-zinc ores of the Akbastau deposit of class –74+45 μm — 100 %

Name	Yeild, %	Content, %		Recovery, %		Conditions of experiment
		Cu	Zn	Cu	Zn	
Cu head	2.74	17.37	3.24	24.85	10.84	Res. CaO in reused water 350 mg/l. To head: Na_2S = 50 g/t; *Kx* = 20 g/t; *T* — 92 = 10 g/t; to rough flotation: *Kx* = 150 (30+120) g/t; T-92 = 10 g/t; Control flotation: *Kx* = 120 g/t
Rough flotation concentrate	17.69	7.33	3.77	67.77	81.51	
Middlings of final recleaner flotation	10.63	0.55	0.20	3.06	2.60	
Tailings	68.94	0.12	0.06	4.32	5.05	
Ore	100.00	1.91	0.82	100.00	100.00	
Cu head	1.71	18.42	3.50	16.58	7.30	The same but with DC-80 instead of T-92
Rough flotation concentrate	11.23	7.63	3.79	45.10	51.95	
Middlings of final recleaner flotation	7.62	0.58	0.22	2.32	2.07	
Tailings	79.94	0.85	0.40	36.00	38.68	
Ore	100.00	1.90	0.82	100.00	100.00	
Cu head	3.09	17.42	4.08	28.24	14.97	The same but with adding to T-92 an equal amount of DC-80
Rough flotation concentrate	16.59	7.40	3.94	64.44	77.65	
Middlings of final recleaner flotation	9.97	0.55	0.20	2.88	2.37	
Tailings	70.36	0.12	0.06	4.43	5.02	
Ore	100.00	1.90	0.84	100.00	100.00	

Thus, investigations of flotation properties of the DC-80 surface-active reagent based on acetylenic alcohols have resulted in the following technological peculiarities of interaction with minerals:

1. A selective complex comprised by cations of nonferrous metals and π-electronic groups of acetylene and ethylene bonds is not an indispensable condition of evincing the additional collecting properties of acetylene-containing flotation reagents on copper-zinc ores. An interaction with acetylene bond only is quite enough.

2. Organo-mineral complex formed by cations of nonferrous metals and π-electronic acetylene bonds possesses surface-active properties which provide the mineralized froth formation.

3. Not only surface hydrophobization of the retrieved minerals and carbonic matters by organic molecules of the surface-active substances guarantees their flotation properties, but surface-active organo-mineral complexes contribute to floating activity increase as well.

4. Acetylene-based reagents demonstrate both selective surface hydrophobization of sulphide minerals and foaming capacity, which allows to provide selectivity and speed of flotation as well as quality of concentrates improvement. The reagent regimes based on DC-80 provide an increase of flotation capacity and efficiency, reduction of material capacity.

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