

A REVIEW OF MODERN FLOTATION COLLECTORS FOR TUNGSTEN MINERALS: FROM BIFUNCTIONAL MOLECULES TO DFT-GUIDED DESIGN (REVIEW)

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Abstract. The flotation efficiency of tungsten minerals depends largely on the structure of the collector and the nature of its adsorption on the mineral surface. Traditional fatty acids, hydroxamates, and organophosphorus reagents are well studied; however, their limited selectivity stimulates the development of more complex molecular systems. *The purpose* of this review is to examine current developments in the collector design for scheelite and wolframite, focusing on the bifunctional, multifunctional, and DFT-guided approaches. A conditional division of the collectors into generations is proposed: from traditional and chelating reagents to bifunctional and multifunctional systems and further to rationally designed collectors, using DFT and molecular modeling. This review examines the collectors containing various combinations of active groups, including amine–hydroxyl, thioether–hydroxamate, bis-hydroxamate, amino–hydroxamate, amidoxime–phosphonate, and hydroxamate–phosphonate systems. Their interactions with the surface Ca, Fe, Mn, and W sites are discussed, as well as the roles of electrostatic attraction, coordination bonding, hydrogen bonding, and hydrophobicity. Particular attention is paid to the increasing application of the density functional theory (DFT), molecular dynamics, electronic structure analysis, and hydrophobicity calculations in the collector design. The current research shows that the computational methods are increasingly being used not only to elucidate the adsorption mechanisms, but also to optimize spacer length, electron donation capacity, hydrophobicity, and ligand combinations prior to or in parallel with the experimental validation. This review focuses on the studies published between 2020 and 2026, with the earlier studies included where necessary to understand the background to the development of the modern approaches to the collector design.

Keywords: tungsten flotation; scheelite, wolframite, flotation collectors, bifunctional collectors, DFT, rational molecular design

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1. Introduction

For Kazakhstan, the development of the tungsten industry has acquired particular significance in recent years. The country possesses one of the world's largest raw material bases for this metal and, according to the official data from the Republic of Kazakhstan, ranks first in the world in explored tungsten reserves [1,2]. The most significant deposits include the Verkhneye Kayraktinskoye and Severny Katpar deposits in the Karaganda region, as well as the Boguty deposit in the Almaty region. The commencement of the industrial development of the Boguty deposit and the development of the capacity for the further processing of tungsten concentrate indicate a renewed interest in the creation of a full-fledged processing chain for the tungsten-containing raw materials in Kazakhstan [3,4]. Under these conditions, improving tungsten-ore beneficiation technologies, including the development of more efficient and selective organic flotation collectors, is of significant scientific and practical interest.

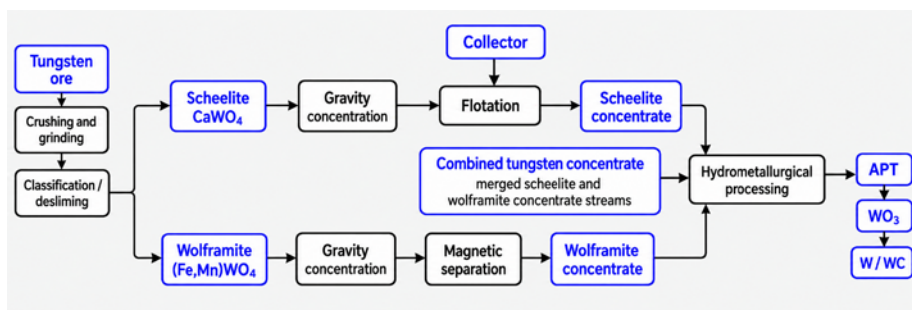


Figure 1 – General beneficiation routes for tungsten minerals.

To understand the place of flotation enrichment in the overall process chain of processing the tungsten-containing raw materials, it is important to consider the mineralogical form of tungsten and the corresponding methods of its extraction. The main industrially significant minerals are scheelite CaWO₄ (~ 70% of the world's tungsten resources) and wolframite (Fe/Mn)WO₄ (~ 30%), for which different, but often combined, enrichment schemes are used [5-7]. In general, the main stages of processing tungsten ores - from crushing and classification to obtaining a concentrate and subsequent hydrometallurgical processing - are presented in Figure 1. A special place in this scheme is occupied by the flotation of the scheelite-containing ores, the efficiency of which is largely determined by the choice of a collector.

The choice of a collector for the flotation of tungsten minerals is determined by its ability to simultaneously ensure a strong interaction with the target mineral surface and sufficient hydrophobization of the particles. Historically, relatively simple organic reagents have been used for these purposes - primarily fatty acids and their salts, classical hydroxamic acids, and individual organophosphorus compounds [8-10]. Oleic acid and oleates, benzohydroxamic and

octylhydroxamic acids, which remain convenient model and industrially significant collectors to this day [11], have been used.

To systematize modern approaches to the development of flotation reagents, this review proposes to consider organic collectors for tungsten minerals as several sequential stages of their molecular evolution. This division is conditional and primarily reflects the evolution of approaches to molecular design: from traditional reagents to chelating agents, then to bi- and polyfunctional systems, and to rational design using DFT and molecular modeling. Moreover, these areas may develop in parallel and partially overlap.

The 1st generation –traditional collectors. Fatty acids and their salts, primarily oleic acid and oleates. They are characterized by a high collecting capacity but limited selectivity.

The 2nd generation – chelating collectors. Hydroxamates, oximes, amidoximes, and simple organophosphorus reagents. Their advantage lies in their more specific coordination interactions with the surface Ca, Fe, and Mn centers.

The 3rd generation – bi- and polyfunctional collectors. The molecules containing two or more active moieties, such as hydroxamate–phosphonate and amidoxime–phosphonate. Such reagents provide multi-site binding to the mineral surface and potentially higher selectivity.

The 4th generation – rationally designed and environmentally oriented systems. The collectors whose structure is optimized using DFT, adsorption modeling, and molecular dynamics, simultaneously taking into account selectivity, reagent consumption, and environmental safety. Traditional fatty acid and classical chelating collectors, primarily hydroxamates and organophosphorus reagents, have already been reviewed in considerable detail in the literature [12–15]. Therefore, the main focus of this review is on more modern approaches –bi- and polyfunctional collectors and their rational molecular design.

Currently, DFT calculations, molecular modeling, and electronic structure analysis are increasingly being used directly in the development and interpretation of the mechanism of action of new collectors [16–22]. Therefore, the boundary between the generations III and IV is becoming largely arbitrary: many bi- and polyfunctional reagents are simultaneously objects of computationally-directed design. Therefore, in this review, generations III and IV are considered together – as a single direction for the multifunctional and rationally designed collectors.

The novelty of this review lies in its examination of collectors for the flotation of tungsten minerals from the perspective of the evolution of molecular design principles – from bi- and polyfunctional reagents to systems, including those rationally designed using DFT. Particular attention is paid to the relationship between molecular architecture, electronic and spatial characteristics, interaction with the mineral surface, and flotation selectivity.

2. Materials and Methods

To prepare this review, a search of scientific literature on modern flotation collectors for tungsten minerals has been conducted, using Scopus, Web of

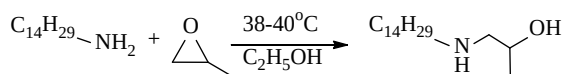
Science, ScienceDirect, and Google Scholar databases. The focus has been on publications made between 2020 and 2026; the earlier studies have been included in the analysis if they represented the initial research on traditional collectors, adsorption mechanisms, or the development of modern approaches to molecular design. The information on the status and development of the tungsten industry in Kazakhstan, deposits, and projects for processing tungsten-containing raw materials has been obtained from the official information resources of the Government of the Republic of Kazakhstan and the Gov.kz portal.

3. Results and Discussion

One of the key research directions is the creation of collectors with multiple functional sites, providing a more selective interaction with the surface of tungsten minerals. Bifunctionality can combine two coordination-active moieties or a chelating site with an auxiliary group that enhances adsorption and hydrophobization. DFT and molecular modeling allow the identification of the reactive sites and the evaluation of their interactions with the Ca, Fe, and Mn sites [23,24].

In this review, a distinction should be made between bi- and polyfunctional collectors, which are individual molecules with several functional centers, and multiligand or multicomponent systems in which the functional interaction is realized between several chemical components. The latter are not bifunctional collectors in the strict molecular sense, but are considered here as a further development of the principle of cooperative interaction of several functional centers with a mineral surface.

One early example of a functionally bifunctional approach is N-tetradecylisopropanolamine (NTIA), which combines an amine and a hydroxyl site. NTIA has been prepared by the addition of tetradecylamine (TDA) to propylene oxide in anhydrous ethanol at 38–40°C (Scheme 1) [25].



Scheme 1 – The synthetic route of NTIA.

The protonated amine center provides predominantly an electrostatic interaction with the negatively charged surface of scheelite, while the OH group is involved in hydrogen bonding [25,26]. Using ethetraditional collectors DDA (dodecylamine) and NaOL (sodium oleate), the WO₃ content in the concentrate has been 40.44 and 39.60%, respectively, while the use of NTIA at pH 7.0 and a concentration of 50 mg/L increased this figure up to 62.56% with a recovery of 96.44%, confirming its higher efficiency and selectivity in scheelite flotation (Figure 2).

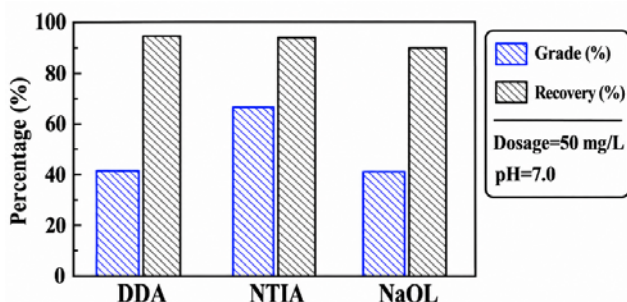


Figure 2 – The flotation performance of DDA, NTIA, and NaOL.

A more pronounced cooperative effect is realized in 2-(benzylthio)aceto-hydroxamic acid (BTHA) [27], applied for the separation of wolframite and fluorite [28]. BTHA combines the thioether and hydroxamate moieties, which are jointly anchored on Fe-centers of the wolframite surface to form the Fe–S bonds and a five-membered hydroxamate-(O,O)-Fe complex (Figure 3). The DFT analysis has identified S- and O-atoms as the main reaction centers, and the MD modeling has shown a significantly stronger interaction of BTHA with wolframite (–128.90 kJ/mol) than with fluorite (–10.84 kJ/mol). The obtained calculated data have been confirmed by the flotation tests and XPS, demonstrating the efficiency of combining bifunctional design and computational prediction of the collector selectivity.

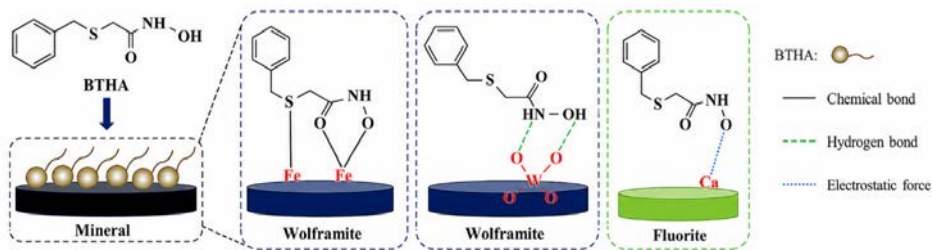
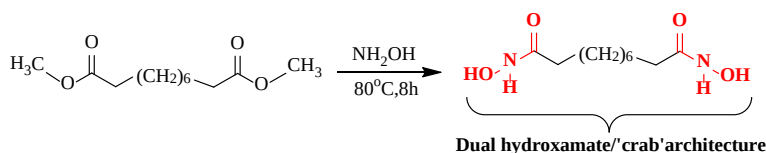


Figure 3 – The proposed interaction mechanism of BTHA with wolframite and fluorite.

Another type of bifunctional design is represented by sebacoylhydroxamic acid (SHA), which contains two hydroxamate groups (Scheme 2). In the work of Zhang et al. [29], it has been shown that SHA, due to its “crab” structure, provides a high extraction of wolframite without Pb^{2+} activation [29], and outperforms the traditional BHA/ $Pb(NO_3)_2$ system [30], which is especially important considering the toxicity and bioaccumulation of lead [31–33]. In later studies [34,35], the mechanism of action of SHA has been further investigated by XPS and DFT methods. The two $-C(O)NHOH$ groups interact preferentially with the Fe centers of the wolframite surface to form five-membered chelate rings, and

a smaller HOMO–LUMO gap compared to BHA (0.1557 vs. 0.2132 a.u.) indicates a higher reactivity of SHA [35].



Scheme 2 – The synthetic route of SHA.

A similar bis-hydroxamate design has been implemented for DHA (dodecanediohydroxamic acid), for which DFT confirmed the high reactivity of both hydroxamate groups [36].

For scheelite, a promising example is N-(3-(octylamino))hydroxamic acid (NOHA), developed as an efficient amphoteric collector for scheelite enrichment without a prior activation by $\text{Pb}(\text{NO}_3)_2$ [37]. At pH 8.0 and a concentration of $2.0 \times 10^{-4} \text{ mol L}^{-1}$, NOHA has provided >95% scheelite recovery without prior Pb^{2+} activation. The molecular design of NOHA is based on the combination of a selective hydroxamate group with an amine center: the hydroxamate moiety provides an interaction with the Ca sites on the scheelite surface, which has been confirmed in a number of studies by DFT and XPS [34,38], while the protonated amino group additionally increases the affinity of the collector for the negatively charged mineral surface and enhances its adsorption [37,39].

A more complex heterobifunctional architecture is realized in the DHAHEP (dihexyl (2-amino-2-(hydroxyimino)ethyl) phosphonate) collector, whose molecule combines amidoxime and phosphonate moieties [40]. According to FTIR, XPS, and DFT data, DHAHEP adheres to wolframite in a mixed manner: the cationic form of the collector predominantly interacts electrostatically with the WO_4^{2-} surface sites, while the amidoxime and phosphoryl centers participate in chemical binding with the surface Fe sites (Figure 4). Thus, DHAHEP combines several adsorption mechanisms in a single molecule, ensuring a high affinity for wolframite and its efficient separation from quartz.

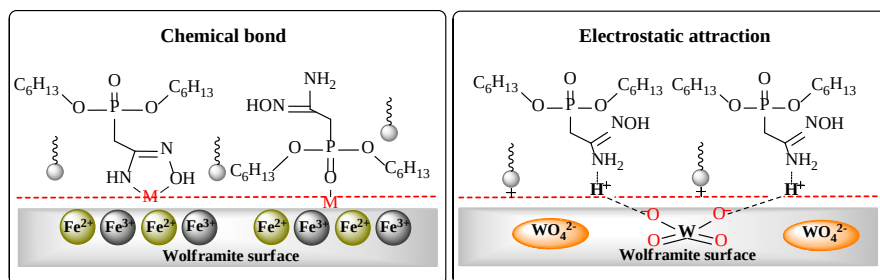


Figure 4 – The proposed adsorption mechanisms of DHAHEP on the wolframite surface: chemical bonding and electrostatic attraction.

Microflotation has demonstrated the high collection capacity of DHAHEP for wolframite: at pH 2–4.5, its recovery has exceeded 90%, while for quartz it has remained below 60%. In a wolframite–quartz mixture at pH ~4 and 8×10^{-5} mol L⁻¹ DHAHEP, the wolframite recovery has been 64.5% at the content of 48.9%.

Another variant of functional interaction is observed for DHHAOEP (dihexyl (2-(hydroxyamino)-2-oxoethyl) phosphonate), a hydroxamate-phosphonate collector of scheelite [41]. Unlike DHAHEP, the P=O group here is practically not directly involved in chemical adsorption: according to XPS and DFT data, binding to the surface occurs predominantly through the hydroxamate fragment. However, DFT has shown that the presence of a phosphoryl group alters the geometry of the active site: the distance between the two O-atoms of the DHHAOEP hydroxamate fragment is 2.889 Å and is almost identical to the distance between the adjacent O-atoms in the surface WO₄²⁻ fragment of scheelite (2.899 Å). This geometric correspondence facilitates the formation of a five-membered surface complex and increases selectivity for scheelite (Figure 5).

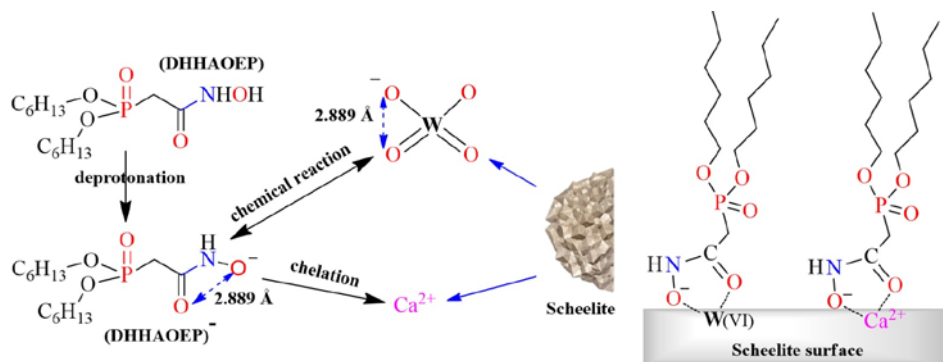


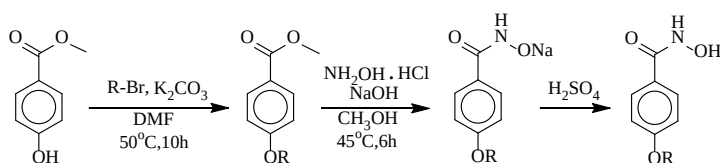
Figure 5 – The proposed adsorption mechanism of DHHAOEP⁻ on the scheelite surface.

Thus, the role of the second functional center in multifunctional collectors can vary significantly: from the direct cooperative coordination binding, as in BTHA [27] and DHAHEP [40], to the structural and electronic optimization of the main chelating center, as in DHHAOEP [41]. These examples clearly demonstrate the importance of DFT and molecular modeling not only for interpreting the adsorption mechanism, but also for rational design of new collectors.

A more direct example of the rational computational design is presented by a series of bifunctional dicarboxyl collectors CS_n for scheelite [42]. In this work, the length of the carbon spacer has been considered as a key parameter determining the relative position of the two carboxyl groups of the collector. TheDFT calculations have shown that the most favorable adsorption on the scheelite surface is characteristic of CS₇, which is associated with a good spatial

correspondence between the carboxyl centers and the Ca sites of CaWO_4 . An analysis of the electron density and charges has confirmed the predominantly ionic nature of the O–Ca interaction. At the theoretical stage, the bifunctional molecule has demonstrated an adsorption energy advantage over single molecules. Further flotation results have confirmed the operating principle of the bifunctional collector structure. This work clearly illustrates the use of DFT at the stage of the targeted collector structure optimization.

Rationally designed systems include the p-alkoxy derivatives of benzohydroxamic acid (AOBHAs), for which the DFT and hydrophobicity calculations have been used for the targeted structure optimization. [43]. For the experimental verification, the four derivatives (MOBHA, EOBHA, POBHA, BOBHA) have been synthesized by sequential alkylation of methyl p-hydroxybenzoate with the corresponding alkyl bromide, subsequent oximation with hydroxylamine, and acidification to yield free hydroxamic acids (Scheme 3). After recrystallization, the purity of the products has exceeded 98%.



Scheme 3 – The synthetic route of AOBHAs.

The alkoxy substituent does not act as an independent coordination center, but due to p- π conjugation it increases the electron-donating ability of the hydroxamate group, while an increase in the length of the alkyl chain enhances the surface hydrophobization (Figure 6). The calculated prediction has been confirmed by the flotation tests, which have shown a consistent increase in the collecting capacity in the series $\text{BHA} < \text{MOBHA} < \text{EOBHA} < \text{POBHA} < \text{BOBHA}$ [43].

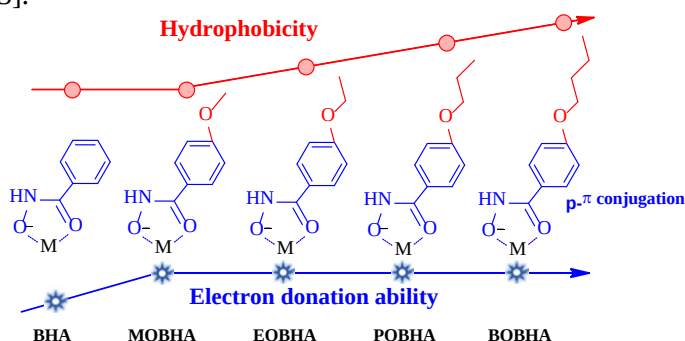


Figure 6 – The structure–property relationship of the p-alkoxy benzohydroxamic acid collectors: hydrophobicity and electron-donating ability.

The subsequent work [44] on the C₃-derived POB, IPOB, and AOB has demonstrated that a higher HOMO energy does not always correspond to better flotation activity: despite the highest electron-donating capacity of IPOB, the more hydrophobic POB has exhibited the highest collecting capacity (Figure 7). These results highlight the need to simultaneously consider both the electronic and hydrophobic characteristics in rational collector design.

It should be noted that individual DFT descriptors, including HOMO/LUMO energies, atomic charges, and interaction energies, are not direct indicators of flotation performance. Their predictive value increases only when solvation, protonation, mineral surface state, and collector hydrophobicity are taken into account jointly. A illustrative example is the POB/IPOB/AOB series, where the highest electron-donating capacity did not correspond to the maximum flotation activity.

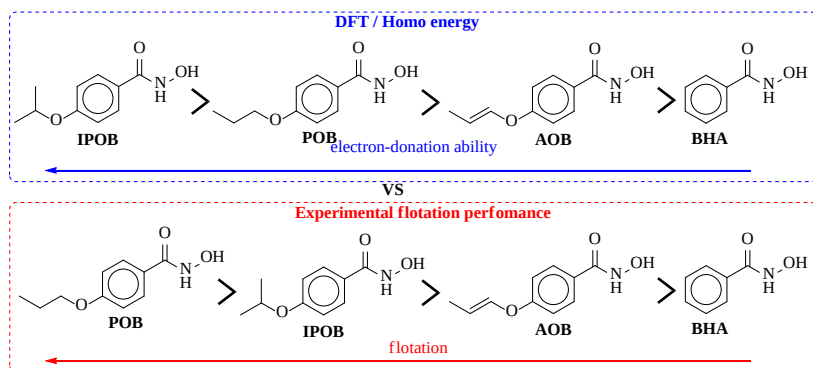


Figure 7 – The DFT-predicted electron-donating ability versus the experimental flotation performance of the C₃ alkoxybenzohydroxamate collectors.

In the work of Deng et al. [45], *m*-methylbenzohydroxamate (3MBHA) has been developed based on BHA. The introduction of a methyl substituent at the meta position has increased the hydrophobicity of the molecule and enhanced its complexation with Pb(II). Compared to BHA, 3MBHA has been characterized by a higher logP and a more pronounced decrease in the surface tension, while a UV–Vis analysis has revealed a stronger interaction with Pb(II) and the formation of a larger number of Pb–hydroxamate complexes. This has been accompanied by an increased adsorption on the scheelite surface and an increase in its flotation recovery. The obtained results demonstrate that the efficiency of hydroxamate collectors can be enhanced by simultaneously optimizing the electronic and hydrophobic properties of the molecule [45].

Another rational design approach considers not only the collector structure but also the chemistry of the specific mineral surface. For the specially selected hydroxamate collector DPHA (N-dodecanoyl-N-phenylhydroxylamine), selectivity in the scheelite–calcite system is attributed to a combination of the Ca-

coordinating hydroxamate center, a hydrophobic organic moiety, and differences in the behavior of surface Ca with changing pH [46]. A similar principle has been implemented using the trisiloxane collector AATS (N-(2-aminoethyl)-3-aminopropyltrisiloxane) for the separation of scheelite and calcite, where the correspondence of the cationic amine center to the differences in the charge state of the mineral surfaces plays a significant role [47]. Thus, the object of rational design is no longer only the collector molecule itself, but also its correspondence to the chemical and electrostatic state of the target mineral surface.

A similar surface-targeted approach was implemented for the modified oleate collector Ca-DBOA (α -bromooleic acid), developed for the selective separation of scheelite and calcite. According to AFM, ζ -potential, FTIR, and XPS data, Ca-DBOA chemically adsorbs on scheelite even in the presence of liquid glass, whereas its adsorption on calcite is significantly suppressed [48].

This approach is widely used: it expands the concept of molecular design, where the object of optimization is no longer only the reagent molecule but also the correspondence of its properties to the specific state of the mineral surface [49].

An interesting direction of rational design, standing somewhat apart, is represented by a series of studies by Wei et al. [50–55] on the creation of organometallic and multiligand collectors based on the Pb–BHA system. In the early studies, the structure of Pb–BHA complexes and the features of their adsorption on the scheelite surface have been investigated using XPS and TOF-SIMS [50] (Figure 8, a). Subsequently, the structure of these complexes has been studied in detail in the crystalline state, solution, and at the solid/liquid interface, which has provided a better understanding of the role of Pb(II) and BHA coordination in the formation of an adsorption-active system [51,52] (Figure 8, b). The next step was an introduction of additional organic ligands. Thus, the multiligand systems Pb–BHA–SDS (sodium dodecyl sulfate) and Pb–BHA–CPF (cupferron) have been developed, for which the enhanced adsorption and increased flotation activity have been shown compared to the original Pb–BHA system (Figure 8, c) [53,54].

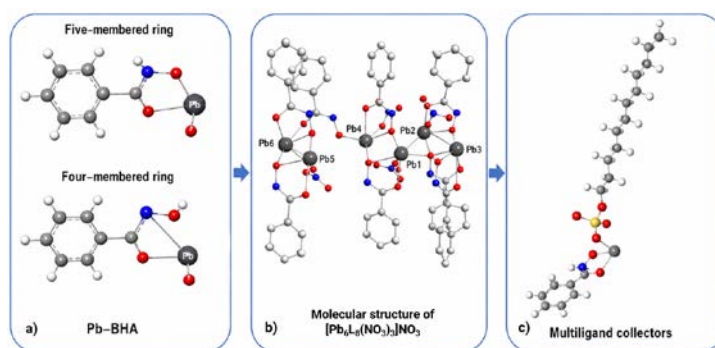


Figure 8 – Evolution of Pb–BHA-based multi-ligand collectors in the studies of Wei et al [50–55].

Further development of this approach has led to the concept of multiple-ligand metal–organic framework collectors (ML-MOF), in which the selection of an additional ligand has been carried out using a quantum chemical analysis, hydrophobicity assessment, and calculations of the interactions with the mineral surfaces. Among the combinations studied, Pb–BHA–SDS and Pb–BHA–OHA have been identified as the most promising, the efficiency of which has been subsequently confirmed by the microflotation tests [55]. Although such systems are not bifunctional collectors in the strict molecular sense, they are conceptually close to them: several functional centers participate in the formation of an adsorption-active system, but belong to different ligands united by a common metal center. In this regard, the multiligand approach can be viewed as a development of the principle of functional cooperation characteristic of bi- and polyfunctional collectors. In this series of studies (Wei et al.), the computational methods have been used at virtually every stage of the concept's development - from the analysis of the electronic structure and adsorption mechanisms to the evaluation of the multiligand complexes and, ultimately, the targeted molecular design of ML-MOFs. As the approach has evolved, the role of DFT has gradually shifted from the interpretation of the experimental data to a tool for the preliminary selection and optimization of the new collector systems.

Another example of a multicomponent design is the Pb–BHA–NaOL system, which, at a component ratio of 6:6:1, provided selective separation of scheelite and calcite at pH 9. The increased selectivity is attributed to the preferential adsorption of positively charged Pb–BHA–NaOL particles on the scheelite surface and their stronger interaction with its surface Ca- and O-sites [56].

To summarize the approaches discussed, the described collectors for scheelite and wolframite, their structural features, adsorption mechanisms, and rational design are compared in Table 1.

Table 1 – Tungsten flotation collectors discussed in this review

Collector [Ref.]	Target mineral	Functional architecture	Main surface site	Main interaction	Computa- tional approach	Pb invol- vement	Design principle
NTIA [25]	Sch	amine–OH	negatively charged sch. surface	electrostatic adsorption + H-bonding	–	No	auxiliary functionality
BTHA [27,28]	Wol	thioether– hydroxamate	Fe	Fe–S bonding + O, O-chelation	DFT, MD	No	cooperative binding
SHA [29,34,35]	Wol	dual hydroxamate	Fe	hydroxamate chelation	DFT	No	dual- hydroxamate design
DHA	Wol	dual	wol. surface	hydroxamate - driven	DFT	No	dual- hydroxamate

[36]		hydroxamate		adsorption			design
NOHA [37]	Sch	amino- hydroxamate	Ca	Ca- hydroxamate chemisorp- tion + amino- assisted adsorption	–	No	amphoteric/c ooperative design
DHAHEP [40]	Wol	amidoxime- phosphonate	Fe/WO ₄ sites	chemical + electrostatic	DFT	No	Heterobifunc- tional design
DHHAOEP [41]	Sch	hydroxamate – phosphonate	Ca / W- containing surface sites	hydroxamate - dominated chemisorp- tion	DFT	No	geometric matching
CS ₇ [42]	Sch	dicarboxylate	Ca	ionic O–Ca interaction	DFT	No	spacer/site matching
AOBHAs [43]	Wol	alkoxy- modified BHA	Pb-activated sites	Pb-mediated hydroxamate adsorption	DFT + logP	Yes	electronics + hydrophobi- city
3MBHA [45]	Sch	methyl- modified BHA	Pb-associated surface sites	Pb- hydroxamate complex formation + adsorption	logP	Yes	electronics + hydrophobi- city
DPHA [46]	Sch	N-substituted hydroxamate	Ca	selective Ca coordination	DFT	No	pH- and surface- specific design
AATS [47]	Sch	diamino- trisiloxane	negatively charged sch. surface	electrostatic adsorption via protonated amino group	DFT	No	surface- charge matching
Ca-DBOA [48]	Sch	modified oleate	sch. surface / Ca-related sites	selective chemisorp- tion; suppression on calcite by water glass	–	No	surface- targeted modification
ML-MOF [50-55]	Sch, Wol	Pb–BHA + multiple ligands	mineral surface sites	metal- mediated multiligand adsorption	quantum- chemical screening	Pb- containin g system	multiligand design

Pb-BHA- NaOL [56]	Sch	self- assembled Pb-BHA- oleate system	O / Ca sites	chemical + electrostatic adsorption	–	Pb- containin g system	self- assembled multicompo- nent design
Note - Sch – scheelite, Wol – wolframite							

4. Conclusion

The analysis shows that the modern development of flotation collectors for scheelite and wolframite is primarily associated with a shift from the selection of individual functional groups to the targeted design of the entire molecular architecture of the reagent. High efficiency is determined not by the number of functional centers per se, but by their chemical nature, spatial arrangement, and ability to interact with the active sites on the mineral surface.

For bi- and polyfunctional collectors, several main modes of action can be distinguished: the coordinate binding of several centers, the combination of the main chelating moiety with an auxiliary group that enhances adsorption, and the structural and electronic influence of the second moiety on the geometry and reactivity of the main center. Therefore, functional cooperation is becoming a more important parameter than the formal number of donor groups in the molecule.

A separate selectivity factor is the spatial correspondence of the collector's active centers to the surface Ca, Fe, Mn, and W sites.

Equally important is the combined consideration of electronic and hydrophobic properties. Therefore, rational design should consider a complex set of the interrelated molecule characteristics, rather than a single descriptor.

DFT, molecular modeling, and electronic structure and hydrophobicity analysis are now used not only to elucidate the adsorption mechanism after the experiment, but also to pre-select the structure, spacer length, substituents, and composition of the multiligand systems. Thus, computational methods are gradually becoming a tool for targeted design, but their results should be considered in conjunction with the flotation and surface chemistry experiments.

Overall, the most promising direction appears to be the creation of collectors, which simultaneously optimize selective binding to the mineral surface, the spatial organization of the active sites, electronic properties, and hydrophobicity, while also reducing the need for toxic activators. Of particular practical interest are collectors capable of providing high efficiency without preliminary Pb²⁺ activation; however, their direct quantitative comparison requires standardized flotation test conditions. This approach allows for a transition from empirical reagent searches to a more substantiated molecular design, tailored to a specific mineral and its surface properties.

ВОЛЬФРАМ МИНЕРАЛДАРЫНА АРНАЛҒАН ЗАМАНАУИ ФЛОТАЦИЯЛЫҚ ЖИНАҒЫШТАРҒА ШОЛУ: БИФУНКЦИОНАЛДЫ МОЛЕКУЛАЛАРДАН DFT НЕГІЗІНДЕГІ ЖОБАЛАУҒА ДЕЙІН (ШОЛУ)

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Түйіндеме. Вольфрам минералдарын флотациялау тиімділігі көп жағдайда жинағыштың құрылымына және оның минерал бетінде адсорбциялану сипатына байланысты. Дәстүрлі май қышқылдары, гидроксаматтар және фосфорорганикалық реагенттер жақсы зерттелген, алайда олардың шектеулі селективтілігі күрделірек молекулалық жүйелерді әзірлеуге ынталандырады. Осы шолудың мақсаты – бифункционалды, көпфункционалды және DFT-бағытталған тәсілдерге ерекше назар аударып, шеелит пен вольфрамитке арналған жинағыштарды жобалаудағы заманауи әзірлемелерді қарастыру. Біз жинағыштарды шартты түрде буындарға бөлуді ұсынамыз: дәстүрлі және хелаттаушы реагенттерінен бастап би- және полифункционалды жүйелерге дейін және одан әрі DFT және молекулалық модельдеуді пайдалана отырып рационалды жобаланған жинағыштарға дейін. Шолуда белсенді топтардың әртүрлі үйлесімдерін қамтитын, оның ішінде амин–гидроксидті, тиоэфир–гидроксаматты, бис-гидроксаматты, амина–гидроксаматты, амидоксим–фосфонатты және гидроксамат–фосфонатты жүйелер бар жинағыштар қарастырылады. Олардың беткі Са-, Fe-, Mn- және W-сайттарымен әрекеттесуі, сондай-ақ электростатикалық тартылыс, координациялық байланыс, сутектік байланыстар мен гидрофобтылықтың рөлі талқыланады. Жинағыштарды әзірлеуде тығыздық функционалы теориясын (DFT), молекулалық динамиканы, электрондық құрылымды талдаудың және гидрофобтық есептеулердің қолданылуының артуына ерекше назар аударылған. Заманауи зерттеулер көрсеткендей: есептеу әдістері тек адсорбция механизмінен түсіндіру үшін ғана емес, сонымен қатар тәжірибелік тексеруге дейін немесе онымен параллельді түрде спейсер ұзындығын, электрондонорлық қабілеттің, гидрофобтығын және лигандтар комбинацияларын оңтайландыру үшін де барған сайын кеңінен қолданылуда. Шолуда негізгі назар 2020–2026 жылдары жарияланған зерттеулерге шоғырландырылады, сондай-ақ заманауи жинағыштарды жобалау тәсілдерінің дамытудың алғышарттарын түсіну қажет болған жағдайларда ертерек жарияланған жұмыстар енгізілген.

Түйінді сөздер: вольфрам флотациясы, шеелит, вольфрамит, флотациялық жинағыштар, бифункционалды жинағыштар, DFT, рационалды молекулалық жобалау

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ОБЗОР СОВРЕМЕННЫХ ФЛОТАЦИОННЫХ КОЛЛЕКТОРОВ ДЛЯ ВОЛЬФРАМОВЫХ МИНЕРАЛОВ: ОТ БИФУНКЦИОНАЛЬНЫХ МОЛЕКУЛ ДО ПРОЕКТИРОВАНИЯ НА ОСНОВЕ DFT (ОБЗОР)

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Резюме. Эффективность флотации вольфрамовых минералов во многом зависит от структуры коллектора и характера его адсорбции на минеральной поверхности. Традиционные жирные кислоты, гидроксаматы и фосфорорганические реагенты хорошо изучены, однако их ограниченная

селективность стимулирует разработку более сложных молекулярных систем. Цель настоящего обзора – рассмотреть современные разработки в области дизайна коллекторов для шеелита и вольфрамита, уделяя особое внимание бифункциональным, многофункциональным и DFT-направленным подходам. Нами предлагается условное разделение коллекторов на поколения: от традиционных и хелатирующих реагентов к би- и полифункциональным системам и далее к рационально спроектированным коллекторам с использованием DFT и молекулярного моделирования. В обзоре рассматриваются коллекторы, содержащие различные сочетания активных групп, включая амин–гидроксильные, тиоэфир–гидроксаматные, бис-гидроксаматные, амино–гидроксаматные, амидоксим–фосфонатные и гидроксамат–фосфонатные системы. Обсуждаются их взаимодействия с поверхностными Ca-, Fe-, Mn- и W-сайтами, а также роль электростатического притяжения, координационного связывания, водородных связей и гидрофобности. Особое внимание уделено всё более широкому применению теории функционала плотности (DFT), молекулярной динамики, анализа электронной структуры и расчётов гидрофобности при разработке коллекторов. Как показывают современные исследования: вычислительные методы всё чаще используются не только для объяснения механизмов адсорбции, но и для оптимизации длины спейсера, электронодонорной способности, гидрофобности и комбинаций лигандов до или параллельно с экспериментальной проверкой. Основное внимание в обзоре концентрируется на исследованиях, опубликованных в 2020–2026 гг., при этом более ранние работы включены там, где это необходимо для понимания предпосылок развития современных подходов к дизайну коллекторов.

Ключевые слова: флотация вольфрама, шеелит, вольфрамит, флотационные коллекторы, бифункциональные коллекторы, DFT, рациональное молекулярное проектирование

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