

# **Molecular Modelling and Docking Approach for Predicting Potential Flotation Reagents**

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**Abstract** -The molecular models of complexes of poorly studied mineral clusters and reagents in developing the principles of evaluation of forecasting in flotation reagent activity have been created and optimized by using Chem Bio 3D and ChemOffice2005 by Cambridge Soft with optimization by MM2. It is proposed to use structure based virtual screening (SBVS) and reduce enormous amount of chemical compounds to a more manageable number for synthesis and screening which could lead to potential flotation candidates. The metal tellurides and arsenic sulfides as poorly explored types of minerals have been investigated. HOMO, SOMO, LUMO and total energies, atomic charges and s-, p-, d-population were determined for the various compounds. The strategy of prognosis of collector activity evaluation (PCAE) has been proposed as a consistent approach to estimate the interaction between a collector and a mineral cluster to search the analogue of butyl xanthate. The relationship between PCAE and flotability has been established. The results obtained indicate that the lower PCAE the stronger the interaction between the collector and the mineral cluster. The binary complexes of various reagents on the mineral surface have been studied. It was shown that the lowest magnitude of PCAE was obtained for arsenopyrite with binary mixture of dibutyl-aminoethyl dithiophosphoric acid and diethyl-aminoethyl xanthic acid which indicated the high chemical activity of the combination of reagents. Forecasting of perspective flotation reagents by screening of chemical compounds and theoretical results obtained from research can provide a basis for innovative technology in mineral processing.

**Keywords:** flotation, mineral clusters, molecular modeling, collector activity evaluation, forecasting, docking method

## **1. Introduction**

Currently tenths of millions of organic compounds with various chemical structures have been synthesized. Tenths of thousands of chemicals were either tested or suggested as flotation reagents. Each compound has its specific physical and chemical properties. This is the connection between the spatial structure of molecules and chemical activity of the compounds. However the most troublesome question for researchers remains the estimation of quantitative structure-property relationship. The established correlation can be extremely helpful in fast selection of compounds with the desired properties as well as in the synthesis of new reagents. Corporate and commercial libraries have a huge amount of information about organic compounds for data screening. Nevertheless, in practice it is not necessary to check the whole database of these libraries, but basically the information about compounds having the highest ability to react with mineral clusters should be taken into account.

Molecular modeling has been intensively developed over the past ten years. Significant research on computer modeling of oxhydryl reagents was carried out in India (Pradip et al. 2003, Rai 2012). The molecular structures of the various collectors were fully optimized in China using density functional theory (DFT) which offered an effective tool in the calculation of the properties and energies of the various collectors (Liu et al 2008, Liu et al 2012). Molecular modeling of sulphhydryl reagents was carried out in Turkey (Yekeler and Yekeler 2006) and Finland (Porento and Hirva 2004).

In a series of papers the authors have proven the effectiveness of using computer technology and chemical software to study the ore flotation (Solozhenkin 2012a, Solozhenkin 2012b, Solozhenkin and Krausz 2012c, Solozhenkin 2013, Solozhenkin and Ibragimova 2014a). It was proposed a new class of compounds with phosphorus(III) such as  $(C_2H_5)_2PCS_2H$ ,  $(C_2H_5)_2PCOSH$ ,  $(C_2H_5O)_2PCS_2H$ ,  $(C_2H_5O)_2PCOSH$ ,  $(C_2H_5)_2PCSOH$  and  $(C_2H_5O)_2PCSOH$  for platinum and osmium minerals. It has been established that the reagent  $(C_2H_5O)_2PCS_2H$  can be identified as the prospective collector for flotation of platinum and osmium minerals (Solozhenkin 2012b).

Therefore, the present study aims at constructing molecular models of complexes of poorly studied mineral clusters and reagents, for the development of principles of forecasting evaluation in flotation reagent activity. Metal tellurides and arsenic sulfides were used for this investigation, as examples of poorly explored type of minerals. The knowledge obtained from this research work can provide a basis for innovative technology in mineral processing.

## 2. Methods and Objectives

### 2. 1. Computational Methods

In this study the computational modeling of minerals and reagents was performed using Chem Bio 3D and ChemOffice2005 by Cambridge Soft with optimization by MM2. The semi-empirical calculations were provided by MOPAC 2012 in vacuum (Soloviev 2005; Kheif't'e 2012). Molecular structures of metal tellurides clusters were created. The DTF approach was used to determine the optimal molecular structure and to calculate the atomic charge values, the compositions and energies of HOMO, LUMO and SOMO. The docking approach was applied for identifying new potential flotation reagents.

### 2. 2. Objectives

The study was based on mineral models (flotation reagents), named mineral clusters (reagents), as their structures correspond to chemical formulas and the distance between different atoms corresponds to known tabulated data. Metal telluride clusters, such as  $Te_2Pd$ ,  $Ag_4Te_2$ ,  $AuAg_3Te_2$ , and arsenic minerals, such as realgar, orpiment, lollingite and arsenopyrite, have been studied. The following collectors were selected:  $C_4H_9COS_2H$  (BXA),  $(CH_3)_2NCS_2H$  (DMDTCA),  $(C_2H_5)_2NCH_2CH_2OS_2H$  (DEAEXA),  $((C_4H_9)_2NCH_2CH_2OP)_2S_2H$  (DBAEDTPA), 1-phenyl-1H-tetrazole-5-thiol (Tetrzol).

## 3. Results and Discussion

### 3. 1. Molecular Geometry of Mineral Clusters

The structural and optimized 3D models of metal tellurides are shown in Figure 1.

Figure 2 presents the structural and the 3D model for arsenic mineral clusters

Table 1 presents the calculated Mulliken atomic charge values, the number of electrons, the s-, p-, d- populations and the theoretical dipole moments for metal tellurides. It shows that their d-population order is: palladium (8.16891) < gold (9.98235) < silver (9.99986). The Mulliken atomic charge values, the number of electrons, the s-, p-, d- populations, and the dipole moments for arsenic clusters have been determined and their theoretical analysis shows that the increase in

atomic charge is in the following order: lollingite, orpiment, realgar and arsenopyrite. The d-population for sulfur atoms is in the range [-0.098580, -0.101404].

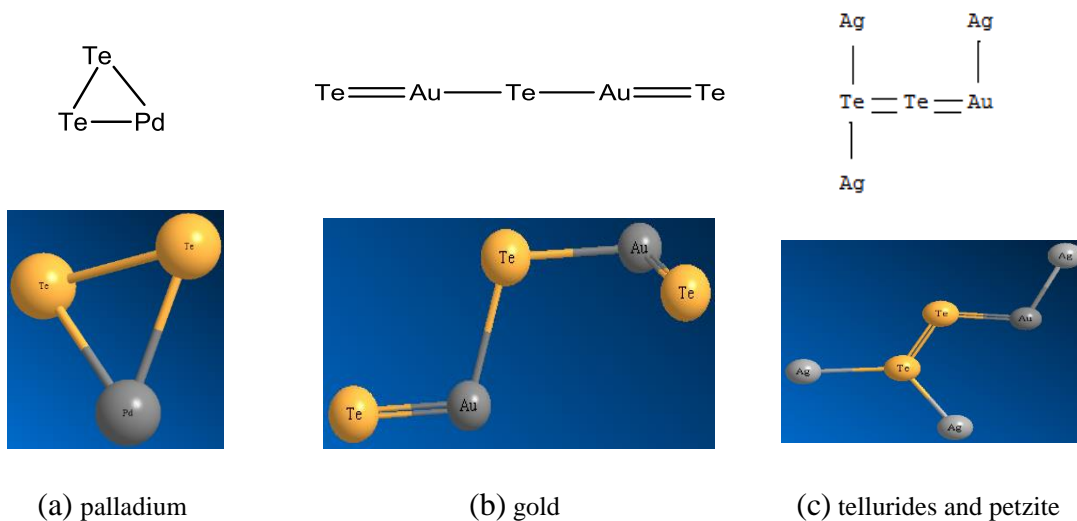


Fig. 1. The structural and 3D models

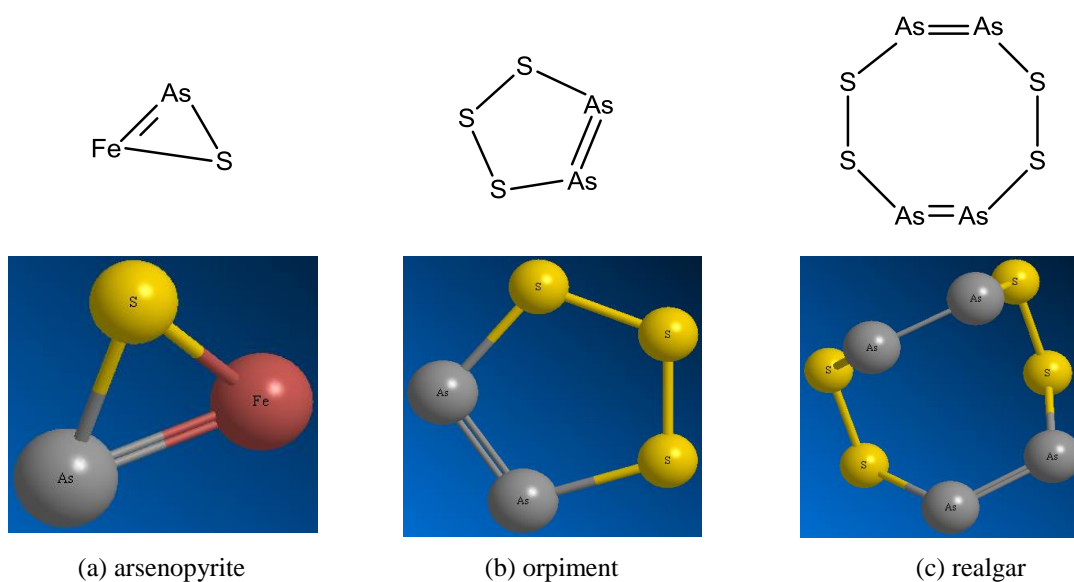


Fig. 2. The optimized structure and 3D models for arsenic mineral clusters

### 3. 2. Structure Based Virtual Screening (SBVS)

Structure based virtual screening of chemical compounds is a fast and accurate method which help to identify potential leads suitable for further development. SBVS has been built up from several steps:

- 1) target and compound library preparation;
- 2) reducing the amount of compounds;
- 3) running the actual docking algorithms;
- 4) post-processing and evaluation;
- 5) ranking the results for assay by scoring function;
- 6) cutting the non-relevant compounds;
- 7) final Hit Selection.

Table. 1. Selected optimized parameters for studied clusters of metal tellurides.

Mineral Cluster	Atom number	Type	Charge	N <sup>o</sup> of electrons	s-popul.	p-popul.	d-popul.
Gold Telluride TeAuTeAuTe	1	Te	-0.004261	6.0043	1.99874	4.00552	9.98235
	2	Au	0.006642	10.9934	1.00302	0.00799	
	3	Te	-0.017554	6.0176	1.99912	4.01843	9.98265
	4	Au	0.032120	10.9676	0.97705	0.00818	
	5	Te	-0.016948	6.0169	1.99917	4.01777	
Dipole 0.669							
PalladiumTelluride Te <sub>2</sub> Pd	1	Te	-0.011770	6.0118	1.91897	4.09280	8.16791
	2	Te	-0.011622	6.0116	1.91896	4.09267	
	3	Pd	0.023392	9.9766	1.80585	0.00285	
Dipole 1.860							
Silver Telluride Ag <sub>4</sub> Te <sub>2</sub> (Ag <sub>2</sub> Te)	1	Ag	0.108798	10.8912	0.89070	0.00064	9.99986
	2	Te	-0.219688	6.2197	1.95181	4.26788	9.99986
	3	Ag	0.109279	10.8907	0.89022	0.00064	
	4	Te	-0.213981	6.2140	1.95200	4.26198	9.99986
	5	Ag	0.107541	10.8925	0.89195	0.00065	
	6	Ag	0.108052	10.8919	0.89144	0.00065	
Dipole 0.111							
Petzite AgAgTe=TeAuAg (AuAg <sub>3</sub> Te <sub>2</sub> )	1	Te	-0.401090	6.4011	1.95039	4.45070	9.97415
	2	Au	0.040381	10.9596	0.96349	0.02198	
	3	Ag	0.221043	10.7790	0.78352	0.02335	9.97209
	4	Te	-0.215326	6.2153	1.95556	4.25977	9.99964
	5	Ag	0.124421	10.8756	0.87485	0.00110	
	6	Ag	0.230571	10.7694	0.77383	0.02337	
Dipole 11.727							

### 3. 3. Complex Formation with the Aid of Computational Docking Technique

Docking as a method of predicting the preferable orientation of one molecule to a second to form a stable complex, was harnessed to identify the relevant candidates for further flotation operations. The total energy and partial atomic charges have been determined to predict the collecting activity of reagents and their combinations.

The strategy of prognosis of collector activity evaluation (PCAE) has been proposed as a consistent approach to estimate the interaction between a collector and a mineral cluster, as a difference between the energy of the complex and the sum of cluster energy and collector energy. The equation is as follows (Pradip et al. 2014, Wu et al. 2014):

$$E = E_{\text{complex}} - (E_{\text{cluster}} + E_{\text{collector}}), \text{ eV} \quad (1)$$

The lower PCAE is, the stronger the ability of the collector to interact with the mineral cluster will be (Solozhenkin 2013; Solozhenkin et al 2014b). Although PCAE cannot play the role as a physico-chemical indicating parameter for the particle being floated, it allows predicting the preferred formation of a stable complex on the mineral surface.

In the present study, the docking method was used to determine the optimal molecular structure of arsenic mineral cluster with collectors. Figure 3 shows the structure (a) and 3D model (b) of the complex between arsenopyrite and butyl xanthate (BX).

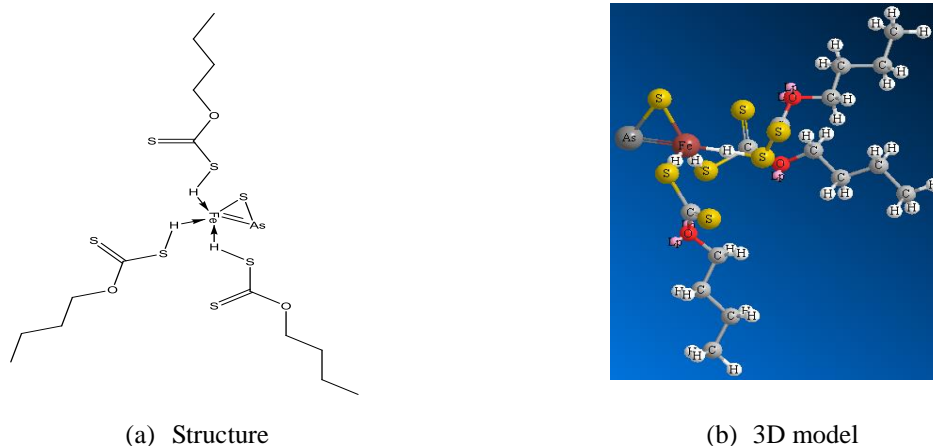


Fig. 3. Arsenopyrite cluster complex with butyl xanthate

Figure 3 indicates that three molecules of BX are attached to the Fe atom of the arsenopyrite. The calculated PCAE data for various arsenic minerals clusters and BX are given in Table 2.

Table. 2. Calculated PCAE for arsenic mineral clusters and butyl-xanthate (BX).

Cluster	Energy, eV			
	Complex	Mineral	Collector	PCAE
1	2	3	4	2 - (3+4)
Arsenopyrite FeAsS	- 4899.66743	- 700.39105	-1397.6974 -1397.6974 -1397.6974	- 6.1854
Lollingite FeAs	- 5498.39366	- 1299.98989	-1397.6974 -1397.6974 -1397.6974	- 5.3128
Orpiment As <sub>2</sub> S <sub>3</sub>	- 4981.65788	- 787.30062	-1397.6974 -1397.6974 -1397.6974	- 1.2662
Realgar As <sub>4</sub> S <sub>4</sub>	- 5415.28451	- 1222.20988	-1397.6974 -1397.6974 -1397.6974	+ 0.0163

Table 2 indicates that the PCAE value decreases from +0.0163 eV for realgar to – 6.1854 eV for arsenopyrite. The lower PCAE value is, the higher floatability of minerals will be. According to Table 2, the increase in floatability for these four arsenic minerals follows this order: realgar, orpiment, lollingite and arsenopyrite, which correlates well with the previous studies (Zhu et al. 2012, Smith et al. 2012).

### 3. 4. Metal Binary Complex Formation

Xanthates are powerful collectors that are commonly used for recovering sulfide minerals. However, their selectivity is low without the use of additional reagents (Liu 2012). It was shown that the highest magnitude of PCAE was obtained for stibnite and kermesite with butyl xanthic acid, which indicated the weak floatability. On the contrary, the application of diethyl-dithio-carbamic acid (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NCS<sub>2</sub>H allowed decreasing to one seventeenth the value of PCAE. This

reagent shows a strong collecting power for stibnite flotation (Solozhenkin and Krausz 2012c). Therefore, the preference of using the combination of reagents above mentioned appears to be significant. It has been established that the recovery of gold with the aid of a combination of reagents was increased and the cyanidation of tailings was avoided (Pshennikov et al. 2014). DEAEX and DBAEDTP are the most prospective reagents for gold telluride flotation. Therefore, the complex and optimized 3D model of gold telluride and the mixture of one molecule of DEAEX and three molecules of DBAEDTP attached to the gold atom were created and the CRE values indicated that this parameter is lower for the individual reagent as compared to the mixture. It was shown that the PCAE value for gold telluride  $Au_2Te_3$  cluster with DEAEX was -302,5969 eV. According to these data, there is a preferable interaction between DEAEX and  $Au_2Te_3$ .

Studies carried out on this subject have also shown that screening chemical compounds can forecast the application of new dialkyl-amino-sulphydril reagents for arsenic mineral flotation. The comparison of the PCAE value between BX and various perspective collectors attaching on the arsenopyrite cluster are given in Table 3.

Table. 3. Calculated PCAE for various complexes.

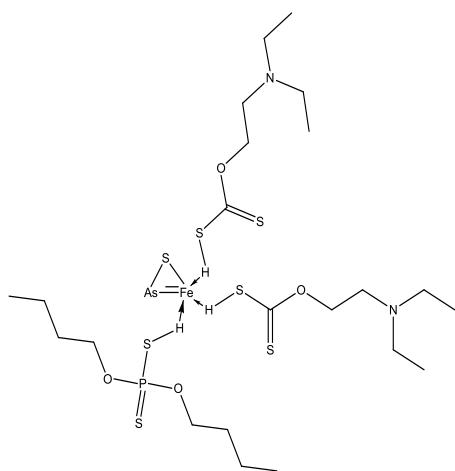
Mineral + collector complex	PCAE, eV	Difference relative to BX
FeAsS + DMDTC	-2.1638	-1.2604
FeAsS + BX	-3.4442	-2.7423
FeAsSStr3BX	-6.1865	0
FeAsSStr3DEAEX	-6.4376	0.2522
FeAsSStrDBAEDTP	-6.1043	-0.0811
FeAsSStr2DEAEX+1DBAEDTP	-6.8385	0.1009
FeAsSStr3Tetrzol	-4.7422	-1.4432

The analysis of Table 3 indicates that the PCAE value decreases in the following order: DMDTC, Tetrzol, DBAEDTP, BX, DEAEX, mixture DEAEX+BX. The lowest PCAE is clearly for the mixture of reagents since this combination of reagents has a PCAE value of -6,8385 which is less than the PCAE value for BX (relative difference equals 0.1009 eV. Based on these calculations, it was suggested to apply the combination of DEAEX and DBAEDTP for arsenopyrite flotation. Figure 4 shows the optimized geometrical structure and the 3D model of the arsenopyrite complex with one molecule of DBAEDTP and two molecules of DEAEX.

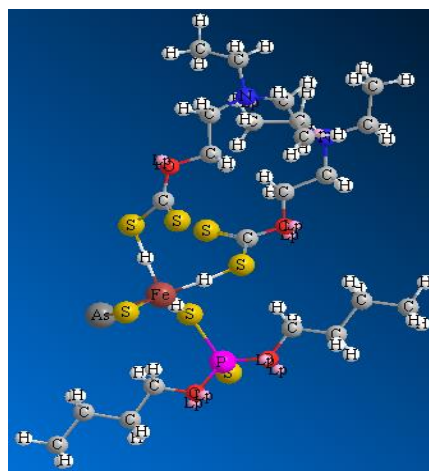
#### 4. Conclusions

1. The molecular models of complexes of poorly studied mineral clusters and reagents in developing the principles of forecasting evaluation in flotation reagent activity have been developed and optimized. The HOMO, SOMO, LUMO energies, the atomic charges, and the s-, p-, d-population on orbitals have been determined.
2. The structure based virtual screening (SBVS) has been proposed to reduce the amount of chemical compounds available to a more manageable number for synthesis and screening which could lead to potential flotation candidates.
3. The strategy of prognosis of collector activity evaluation (PCAE) has been suggested as a consistent approach to estimate the interaction between a collector and a mineral cluster. The lower PCAE is, the stronger the interaction between the collector and the mineral cluster will be.

4. Studies carried out on this subject also forecast the application of new dialkylamino-sulphydril reagents for ore flotation.
5. There is a strengthening effect of binary mixture of reagents on floatability of sulfide minerals which mechanism of interaction has been established and technological properties have been forecasted.
6. Forecasting of perspective flotation reagents by screening of chemical compounds and theoretical results obtained from research can provide a basis for innovative technology in mineral processing.



(a) Structure



(b) 3D Model

Fig. 4. The complex of arsenopyrite cluster and a mixture of DBAEDTP + DEAEX

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