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Calculation of topological connectivity index for minerals^①

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[Abstract] Topological method was applied firstly to calculate the topological connectivity index of minerals (TCIM).

The reciprocal of effective atomic refractivity of metal element in minerals was chosen as its valence. The reasonability of TCIM as an activity criterion was tested through comparison of TCIM with two kinds of electronegativity parameter, i. e. ionic percentage and energy criteria of Yang's electronegativity, solubility product, energy criterion according to the generalized perturbation theory and adsorption of flotation reagents on the surface of minerals. The results indicated that TCIM is an effective structural parameter of minerals to study the structure-activity relationship. In addition, different mineral is of different TCIM value, so TCIM brings about convenience in comparison of flotation activity for minerals.

[Key words] topological connectivity index of minerals; minerals; flotation reagents

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1 INTRODUCTION

One of the main goals that people have been devoting to in flotation research is molecular design of flotation reagents of high performance for a known flotation system. Understanding the interaction between flotation reagent and mineral quantitatively plays an important role in this complex flotation system. In fact, the interaction between flotation reagent and mineral has close relationship with the structural indexes of flotation reagents and/or minerals, and conversely these indexes are the basic parameters in designing new flotation reagents. Among them the electronegativity of group proposed by WANG becomes a standard criterion for activity of flotation reagents, and based on it the basic concept for design of flotation reagents is formed^[1]. While few structural index is proposed for minerals, although ΔX^2 according to Pauling's electronegativity is commonly used to characterize the hydrophilicity of minerals, and even becomes a useful parameter in designing flotation reagent for minerals^[2]. Because ΔX^2 always provides repeated values for different minerals, study on the structural index of minerals still presents important concerns. Recently, some interesting works including the energy band model of electrochemical flotation of sulphide minerals have been done to deal with the flotation and flotation reagents^[3~8]. Of note specially is the group connectivity index (GCI), which is a kind of topological structural index to study the quantitative structure property relationship of flotation reagents, and is turned out to be reasonable in characterizing the structures of flotation reagents^[8]. Hence, topological approach becomes a

potential tool in understanding structure-activity relationship. It's regret that there is no analogous parameter deduced according to the topological structure of minerals so far.

The present paper mainly focuses on deducing topological connectivity index for minerals (TCIM) on the base of simplified chemical graph of minerals, and the reasonability of TCIM to characterize the structure of mineral is discussed.

2 CHEMICAL GRAPH OF MINERALS

As well known, cubic and hexagonal close packing structure are the basic structural types of minerals. Spheres with relatively small radii, generally referring to central cation in minerals, can embed into the tetrahedron, octahedra or hexahedron formed by anion ligands, and form the crystal structure of minerals through the above close packing. The properties of minerals closely depend on the interaction between the ligands and central cation. In the viewpoint of graph theory or topology, the structure of minerals can be expressed graphically further and then construct the chemical graph of minerals. A chemical graph symbolized by Gr is defined in graph theory as an ordered pair consisting of two sets $V(Gr)$ and $E(Gr)$ ^[9]

$$Gr = \{V(Gr), E(Gr)\} \quad (1)$$

where elements of $V(Gr)$ are called vertices, and elements of $E(Gr)$, involving binary relations between the vertices, are called edges. The abstract definition of chemical graph can be comprehended as the adjacency relation between atoms making up the compound. The circle structure in a graph is called cir-

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cuit. A graph that has no circuit is called tree. A part of a graph is called sub-graph. A graph whose vertices are connected with each other by edges is named as complete graph, otherwise, called incomplete graph. For a known structure of minerals, if we neglect the adjacent relations between the anion ligands, then the adjacent relationship between central cation and ligands in tetrahedron, octahedra or hexahedron structure forms an incomplete chemical graph. In this graph, every vertex has a value symbolized as δ called valence.

3 CALCULATION OF TOPOLOGICAL CONNECTIVITY INDEX OF MINERALS

3.1 Basic principle of calculation

According to the connectivity theory proposed by Kier et al^[10], if mineral structure is expressed as chemical graph, the complete set of TCIM becomes the specific characterization of properties of this chemical graph, and the overall number of terms of TCIM is fixed to a specific structure of mineral. TCIM of this chemical graph can be further defined as the sum of the mS_j of all sub-graphs.

$${}^mT_t = \sum_{j=1}^{n_m} {}^mS_j \quad (2)$$

It can be symbolized as mT_t , where t is the type of sub-graph, m is the number of the edges of sub-graph, and it is also called the order of sub-graph or connectivity index. The types of sub-graph include the following: 1) atom, $t = a$; 2) bond or edge, $t = b$; 3) path, $t = p$; 4) cluster, $t = c$. Where, n_m is the number of m th order t -type sub-graph, mS_j is defined as

$${}^mS_j = \prod_{i=1}^{m+1} (\delta_j)^{-0.5} \quad (3)$$

where j is the set of edges making up the sub-graph, the number of the multiplied $(\delta_j)^{-0.5}$ is related to the type of sub-graph. The chain type sub-graph has $m+1$ individual $(\delta_j)^{-0.5}$ multiplied, and m is the order of sub-graph. A comprehensive formula for calculating connectivity index is deduced through Eqs. (2) and (3):

$${}^mT_t = \sum_{j=1}^{n_m} \prod_{i=1}^{m+1} (\delta_j)^{-0.5} \quad (4)$$

where n_m is the number of sub-graph having m edges, and $m+1$ is the number of atoms in the sub-graph.

3.2 Definition of valence of vertex

The valences of ligand vertex with clear physical meaning can be found in literatures conveniently^[10, 11]. However, there is no general definition of valence on the central metal element in minerals.

Hence, a set of effective definition of valence should be gotten.

In fact, lots of useful information may be obtained from the regularity of matter property, e. g. atomic refractivity of compounds. For the following reasons, the reciprocal of effective atomic refractivity of metal element in mineral is chosen as its valence in this paper.

Firstly, the refractivity is the measurement of polarization of electrons in atoms, ions or molecules. It represents the mobility of electrons, particularly the electrons at the outer layer under the action of light. The attractive force of atomic nucleus to electrons and the deformability of electron orbits at outer layers mainly determine the refractivity of atoms, ions or molecules. Hence, the refractivity reflects the structural information of the compounds.

Secondly, the effect of neighboring electric field on cations is very smaller than that on anions, so there are relatively more precise methods to calculate refractivity of cations than that of anions, and a set of generally accepted data has been obtained. This brings about convenience in calculation of effective atomic refractivity of central metal elements.

Thirdly, the reciprocal of effective atomic refractivity has analogous meaning with the valence of atoms. If the larger the valence of atom or the reciprocal of effective atomic refractivity is, then the smaller the polarization of electrons in atom will be. For example, $\delta_F = 10 \sim 20$, $\delta_O = 6$, $\delta_S = 0.94$, then the consequence of polarization is $F < O < S$.

At last, a mature calculating method on effective atomic refractivity has been proposed^[12]. The commonly used formula for calculation of the effective atomic refractivity is

$$R = \left[\sqrt{R_a} - \left(\sqrt{R_a} - \sqrt{R_{i+}} \right) \Delta Y \right]^2 \quad (5)$$

where R represents the effective atomic refractivity of an atom in a known bond, ΔY is the discrepancy of force criteria of Yang's electronegativity, R_a and R_{i+} are the atomic refractivity and ionic refractivity respectively.

$$R_a = \left[a \frac{f}{Y} + b \right]^2 \quad (6)$$

$$R_{i+} = \left[c \frac{\sqrt{2n-1}}{Y} + d \right]^2 \quad (7)$$

where f is the largest bond-form capacity of element; the values are $\sqrt{1}$, $\sqrt{2}$, $\sqrt{3}$ corresponding to s, p, d orbitals respectively; n is the number of layers of electron orbits in cations; a , b , c and d are the constants^[12].

The effective atomic refractivities of some commonly seen mineral elements are enumerated in Table 1. For the convenience of comparison, Table 2 lists the first order TCIM and ionic percentage, discrepancy between energy criteria of Yang's electronegativity

Table 1 Effective atomic refractivities and their reciprocals of some commonly seen mineral elements in different bond

Bond	R_a	R_a^{-1}	Bond	R_a	R_a^{-1}
Mg—O	1.158	0.864	Cu—O	4.343	0.230
Al—O	1.767	0.566	Cu—S	6.607	0.151
Ca—O	1.070	0.935	Zn—O	4.318	0.232
Ca—F	0.938	1.066	Zn—S	6.880	0.145
Ti—O	2.819	0.355	Mo—S	8.954	0.111
Mn—O	3.950	0.253	Sn—O	3.831	0.261
Fe—O	4.322	0.231	Pb—O	3.600	0.278
Fe—S	4.668	0.214	Pb—S	7.610	0.131
Ni—S	6.415	0.156	Ag—S	8.914	0.112

Table 2 First order topological connectivity index, discrepancy between energy criteria of Yang's electronegativity and ionic percentage of some minerals

Mineral	Φ	ΔY_E	1T_b	${}^1T_b^{-1}$
ZnS	18.3	4.40	10.84	9.2
FeS ₂	12.0	3.00	13.38	7.5
NiS	12.0	1.90	15.69	6.4
PbS	12.0	6.20	17.10	5.8
Ag ₂ S	9.0	2.60	18.49	5.5
MoS ₂	12.0	1.90	18.58	5.4
CuFeS ₂	8.6	3.00	21.23	4.7
CaF ₂	89.5	15.90	2.450	40.8
CaCO ₃	79.0	13.50	2.533	39.2
MgCO ₃	73.3	11.60	2.635	38.0
Al ₂ O ₃	63.2	10.60	3.256	30.7
CaWO ₄	79.0	13.50	3.378	29.6
TiO ₂	63.2	9.20	4.111	24.3
SnO ₂	51.4	10.30	4.795	20.9
Fe ₂ O ₃	51.4	8.00	5.096	19.6
Cu ₂ (OH) ₂ CO ₃	47.3	4.60	5.108	19.5
MnWO ₄	51.4	4.35	6.493	15.4

of the basic elements in minerals.

4 REASONABILITY OF TCIM AS ACTIVITY CRITERION

4.1 Correlation of TCIM with electronegativity parameters

Although ionic percentages of minerals may pro-

vide repeated values for different minerals sometimes, they are the basic property parameters of minerals. As we known, the percentage of covalent bond has approximate positive dependency on the hydrophobicity of minerals. In other words, the ionic percentage is the measurement of hydrophilicity of minerals. Hence, it is a significant parameter in understanding Quantitative Structure Activity Relationship (QSAR) of reagent-mineral system.

Table 2 enumerates the ionic percentages and the first order TCIMs of typical sulphide minerals and oxide minerals. Through the comparison, we may find certain correlation between them. A good linear correlation between ionic percentage and the reciprocal of TCIMs exists (see Fig. 1), and the regression equation can be expressed as

$$\Phi = 2.17228 \times 10^2 \times {}^1T_b^{-1} + 1.87338$$

$n = 17, sd = 7.73474, r = 0.96622$

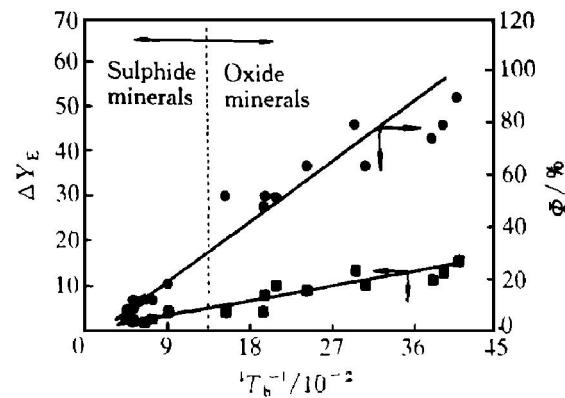


Fig. 1 Dependence of ionic percentage and discrepancy of energy criterion of electronegativity (ΔY_E) on TCIM of minerals

At the same time, we can see from Table 2 and Fig. 1 that different mineral almost has different TCIM value, and the reciprocals of TCIMs of sulphide minerals are generally smaller than that of oxide minerals. Therefore, TCIM can be simply used as parameter to distinguish the mineral types and to approximately tell hydrophobicity of minerals. The mineral with lower TCIM value has stronger hydrophilicity. This result is also supported by comparison between the reciprocal of TCIM and the discrepancy of energy criteria of Yang's electronegativity (ΔY_E) of main elements constituting the minerals.

In the viewpoint of Yang's theory of electronegativity^[12], ΔY_E measures the energy effect from the primary bond polarization in minerals, and is the normalized expression of deviating index of bond energy, reflects the energy characteristics of bond polarization. The square of ΔY_E approximately equals to the formation enthalpy of bond ionization. On the other hand, the bond polarizing energy decides not only the intrinsic properties but also the surface properties of minerals. It is generally accepted that the floatability

of minerals has dependence on the physical and chemical properties of mineral surface, particularly the unsaturated bond energy formed through the destruction of mineral crystal structure.

Indeed, the linear correlation between ΔY_E and reciprocals of TCIM (see Fig. 1) exists also.

$$\Delta Y_E = 0.3305 \times 10^2 \times {}^1T_b^{-1} + 1.05661$$

$$n = 17, \text{sd} = 1.72171, r = 0.93155$$

4.2 Comparison of TCIM with solubility and energy criterion

Another evidence to support TCIM is the solubility product of chemicals, which may be formed through the reaction between flotation reagent and surface ion of minerals. The solubility product hypothesis proposed by Targgart postulates that the flotation reagent with smaller solubility product through interaction with the surface cations of minerals would have stronger flotation activity to these minerals. According to this postulation, TCIMs may also be of certain relationship with solubility product of chemicals for the same flotation reagent. Fig. 2 discloses the linear correlation between the first order TCIMs and the corresponding solubility products. So we believe that the forecasting results by TCIM for flotation activity of minerals will approximately agree with that of solubility product hypothesis.

Similarly, Fig. 2 also reveals the correlation of the first order TCIM with energy criterion, which is a comprehensive quantitative criterion based on the generalized perturbation theory. Energy criterion has taken into accounts of the comprehensive effects of several molecular orbital indices, including frontier orbital energy (E_i), charge density of frontier orbit (ρ_{occ} , ρ_{uocc}) and net charge density (Q) in a formula as the following expression^[1, 13]

$$\Delta E_T^{RL} = \Delta E_1^{RL} + \Delta E_2^{RL} + \Delta E_3^{RL} \quad (8)$$

where ΔE_T^{RL} represents the total energy change; ΔE_1^{RL} , ΔE_2^{RL} , ΔE_3^{RL} represent the energy contribu-

tion of electrostatic effect, positive coordination covalent bond effect and feedback covalent bond effect respectively. Usually, ΔE_T^{RL} has positive dependence on the flotation activity, and reflects the capability of flotation reagent to a mineral.

4.3 Relationship of TCIMs with adsorption of flotation reagents on surface of minerals

Table 3 reveals the adsorption of sodium ethyl xanthate and sodium dodecyl sulfonate on the surface of minerals with different polarity. The adsorption of reagents on surface of mineral is one of the important experimental parameter to measure the flotation activity. The results indicate that the adsorption of reagents for sulphide minerals has positive dependence on TCIM, instead of negative dependence for reagents for oxide mineral. The comparison results also support the approximately linear correlation between the logarithm of adsorption and TCIM. So the flotation activity changes with TCIM exponentially for a definite flotation reagent. In addition, different mineral has different TCIM value, and this brings

Table 3 Adsorption of ethyl xanthate (EX) and sodium dodecyl sulfonate (DS) on surface of different minerals

Mineral	Adsorption/ (mg·m ⁻²)		1T_b
	EX	DS	
CaF ₂	0.75	—	2.450
CaCO ₃	—	6.78	2.533
Fe ₂ O ₃	1.58	4.27	5.096
ZnS	3.57	3.39	10.84
FeS ₂	4.06	3.18	13.38
PbS	7.55	—	17.10
CuFeS ₂	11.20	2.65	21.23

The data of adsorption come from the experimental results in Ref. [7]

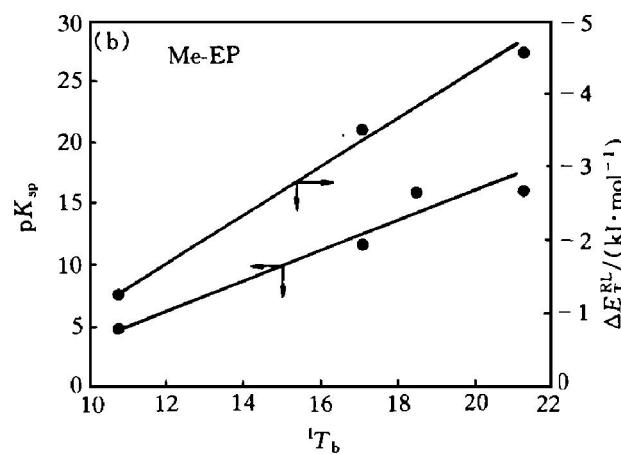
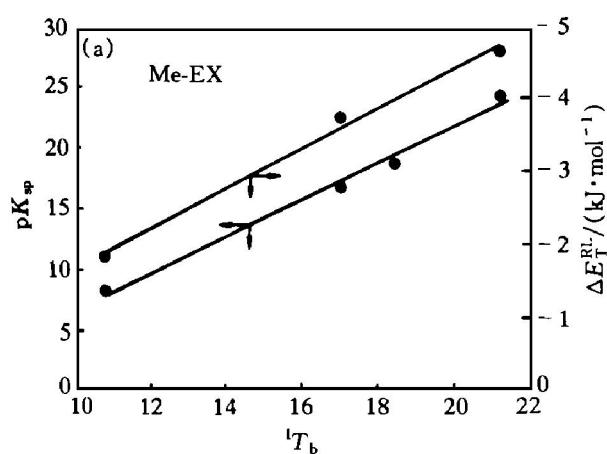


Fig. 2 Dependence of solubility products of several ethyldithiocarbonic salts and diethyl dithiophosphoric salts and energy criterion on TCIM of corresponding minerals

1—Zn(ZnS); 2—Pb(PbS); 3—Ag(Ag₂S); 4—Cu(CuFeS₂)

about convenience in comparison of flotation activity for different minerals.

5 CONCLUSIONS

1) The approach to calculating the topological connectivity index of minerals (TCIM) is proposed. The basic thinking for proposing TCIM is accepted that the complete set of TCIMs is fixed to specific characterization of the structure of minerals. This reveals the probability to use numerical parameter TCIM to characterize the structure and flotation activity of minerals.

2) The reciprocal of effective atomic refractivity of metal element in minerals can be chosen as its valence. The reasonability is discussed by comparison of the physical meaning of effective atomic refractivity and valence of vertex. Hence the computation results of TCIMs are reliable in some degree.

3) TCIM is an effective structural parameter of minerals. The investigation reveals the correlation of TCIM with electronegativity parameters such as ionic percentage and energy criteria of Yang's electronegativity, solubility product, energy criterion according to the generalized perturbation theory and adsorption of flotation reagents on several sulphide and oxide minerals respectively.

4) We always can find some quantitative correlation between the topological structural parameter, e.g. TCIM and the properties of flotation reagent or minerals. The order of TCIM investigated in this paper is only one. Great aids might be brought about by using topological approach to study of flotation system. In addition, the combination of topological indices with quantum chemical parameter may also be a helpful tool in understanding quantitative structure activity relationship of flotation system.

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