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Developing new reagent for selectively precipitation of molybdenum from tungstate solution①

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Abstract: Based on the difference of microscopic properties between MoS_4^{2-} and WO_4^{2-}, a series of new reagents, CuS, NiS, CoS, PbS, HgS, as well as ZnS, were developed for separation of molybdenum from tungstate solution. GPT(Generalized Perturbation Theory) calculation reveals they are more reactive with MoS_4^{2-} than WO_4^{2-}. In laboratory test, CoS, NiS and CuS can remove more than 99.3% Mo. PbS and FeS are also effective for precipitation of Mo, but HgS and ZnS are almost useless. Taking environment and economy factors into consideration, CuS is chosen as the most suitable reagent.

Key words: tungsten; molybdenum; separation; precipitate
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1 INTRODUCTION

Molybdenum and tungsten show very similar chemical properties owing to: 1) they are all located at the ⅥB column in the periodic table of elements and 2) the "lanthanide contraction" makes the radii of Mo^{6+} and W^{6+} (Zr^{4+} and Hf^{4+}, Nb^{5+} and Ta^{5+}) almost equal to each other. This brings about the difficulty of separating the element groups in practice[1].

Unfortunately, impurity Mo in semifinished product of tungsten metallurgy is very strict. In fact, the China National Standard (GB10116-88-0) for ammonium paratungstate(APT) has limited the mass ratio of Mo to WO_3 to a value lower than 2×10^{-5}. So separating molybdenum from tungstate remains a inevitably difficult task for tungsten metallurgist.

Many new ways have been tried[2-7], but there is still not a process which is sound both technologically and economically. This paper presents a brief introduction of our work on Mo/W separation.

2 QUANTUM CHEMISTRY CALCULATION RESULTS OF WO_4^{2-} AND MoS_4^{2-}

Several processes utilized the difference in affinity towards sulfur to separate molybdenum from tungstate solution. By those methods, MoO_4^{2-} is firstly sulfurized into thiomolybdate using $(NH_4)_2S$ or Na_2S, and then removed through classical processes such as precipitation, extraction or ion exchange[2-7].

Little is known about the cause of changes in property of molybdenum after sulfurization though such changes have been proved to be useful in practice. Recurring to the *ab initio* method of quantum chemistry, the microscopic property of WO_4^{2-} and MoS_4^{2-} is studied in this work.

All calculation are carried out using HF(Hartree-Fock) method and LANL2DZ basis set of Gaussion98W software. The calculation includes geometry optimization and single point energy calculation.

Some interesting results, especially those relative to HOMO(highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) are listed in Table 1 and shown in Fig. 1.

It can be seen from Table 1 that the E_{HOMO} of MoS_4^{2-} is much higher than that of WO_4^{2-} (the energy difference is up to 4.85 eV), indicating that electrons in the HOMO of MoS_4^{2-} are more liable to escape. So it is plausible to consider that MoS_4^{2-} is more coordinate than WO_4^{2-} since the frontier orbits(HOMO and LUMO) play the predominant role in chemical reaction[8].

Table 1 also shows that the HOMO of MoS_4^{2-} and WO_4^{2-} are composed of atomic orbits of S and O, respectively. So MoS_4^{2-} will mainly show properties of sulfur while WO_4^{2-} acts as oxygen when participating in a chemical reaction.

3 SELECTION OF NEW REAGENT FOR REMOVING MOLYBDENUM FROM TUNGSTATE SOLUTION

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Collectors such as xanthate and aerofloat used for floatation of sulfide are reagents containing sulfhydryl and/or thipcarbonyl. As MoS_4^{2-}, the function groups are also mainly composed of sulfur atom orbits. So it is reasonable to take MoS_4^{2-} as a special collector, which possess hydrophilic functional group that provides selectivity but no hydrophobic one that shows floatation ability. However, we do not want to use it as a collector. On the contrary, we can select a series of sulfides and use them as reagents for removing molybdenum from tungstate solution.

CoS, NiS, FeS, CuS, PbS, HgS and ZnS are selected as potential reagent that can selectively react with MoS_4^{2-} in tungstate solution.

4 REACTIVITY OF SULFIDES WITH MoS_4^{2-}

4.1 Qualitative analysis of reactivity of sulfides with MoS_4^{2-}

Generally when nucleophilic reagent reacts with electrophilic reagent, the frontier orbits which play a predominant role are the HOMO of nucleophilic reagent and the LUMO of electrophilic reagent. According to the frontier orbital theory[8], the smaller the orbital energy gap between the nucleophilic reagent's HOMO and the electrophilic reagent's LUMO, the more easily they react with each other. If the energy gap exceeds 6.0 eV, the reaction can hardly go on.

The data about HOMO and LUMO (In fact, the LUMO here means virtual molecular orbital) for those sulfides are listed in Table 2.

From the results shown in Table 1 and Table 2, one can find that the energy gaps between HOMO of WO_4^{2-} and LUMO of sulfides are all larger than 9.0 eV. On the contrary, for MoS_4^{2-} and these sulfides, this value are all less than 6.0 eV. So we expect that MoS_4^{2-} is easy to react with sulfides but WO_4^{2-} will hardly do so.

4.2 Half-quantitative analysis of reactivity of new reagent with MoS_4^{2-}

When a nucleophilic molecule S reacts with an electrophilic molecule T, the system will release or absorb some energy (ΔE). Using General Perturbation Theory (GPT), Klopmam[9] established a formula to calculate ΔE. With several approximation processes, an approximate formula is derived from Klopmam's research work. Provided that atom a in molecule A and atom b in molecule B interact directly in the reaction of molecule A and molecule B, the formula can be depicted as follows:

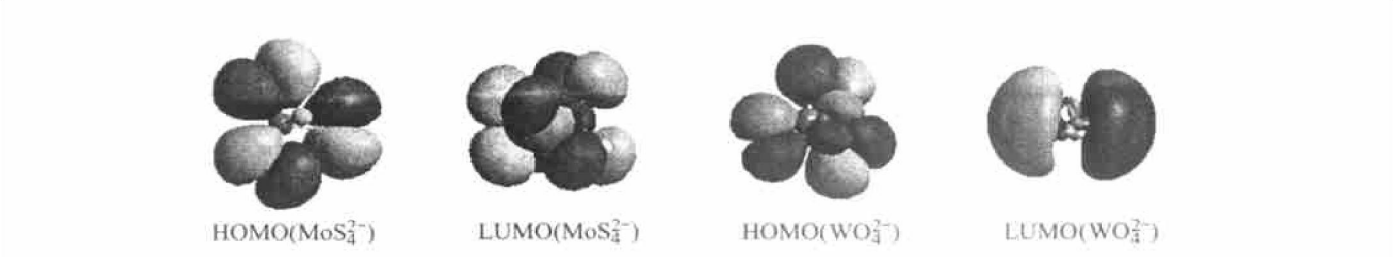

Fig. 1 Frontier orbit pictures of MoS_4^{2-} and WO_4^{2-} molecules

Table 1 Quantum chemistry calculation results of WO_4^{2-} and MoS_4^{2-}

Species	E_{HOMO}/ hartree	E_{LUMO}/ hartree	ρ^M_{HOMO}	ρ^R_{HOMO}	ρ^M_{LUMO}	ρ^R_{LUMO}	q_M	q_R	Ion radius / Å
WO_4^{2-}	- 0.387 93	- 0.002 78	≈0	0.265 6	0.967 8	≈0	1.73	- 0.93	3.54
MoS_4^{2-}	- 0.209 59	- 0.010 91	≈0	0.222 6	0.714 6	≈0	- 0.03	- 0.49	4.50

E_{HOMO} is the energy of highest occupied molecular orbital, E_{LUMO} is the energy of lowest unoccupied molecular orbital, hartree is the atomic units of energy, 1 hartree = 27.211 6 eV; ρ^M_{HOMO} and ρ^R_{HOMO} are the electron densities in HOMO of metal atom M and ligand atom R, respectively; ρ^M_{LUMO} and ρ^R_{LUMO} are the electron densities in LUMO of metal atom M and ligand atom R, respectively; q_M and q_R are the atomic charges of metal atom M and ligand atom R in molecular.

Table 2 Some important calculation results of metal sulfides

Sulfide	E_{HOMO}/ hartree	E_{LUMO}/ hartree	ρ^M_{HOMO}	ρ^R_{HOMO}	ρ^M_{LUMO}	ρ^R_{LUMO}	q_M	q_R
CoS	- 0.297 72	- 0.015 92	0.029	0.561	0.655	0.093	0.379	- 0.379
NiS	- 0.282 38	0.034 70	0.697	0.012	0.947	0.096	0.04	- 0.04
FeS	- 0.319 79	- 0.048 53	0.095	0.435	0.656	0.133	0.427	- 0.427
CuS	- 0.334 55	- 0.009 58	0.027	0.571	0.695	0.088	0.350	- 0.350
PbS	- 0.333 63	- 0.000 80	0.067	0.588	0.626	0.224	0.606	- 0.606
HgS	- 0.335 68	- 0.055 34	0.024	0.794	0.408	0.315	0.293	- 0.293
ZnS	- 0.323 65	- 0.056 87	0.027	0.533	0.501	0.237	0.506	- 0.506

$$\Delta E = -\frac{q_a q_b}{R_{ab}\varepsilon} + \frac{\rho^a_{HOMO}\rho^b_{LUMO}}{2(E^A_{HOMO} - E^B_{LUMO})} \cdot \exp[-\frac{1}{2}(x_a - x_b)^2]$$

where q_a and q_b are the charges respectively of atoms a and b; R_{ab} is the distance between atoms a and b after molecules A and B react each other; ε is the dielectric constant of the medium; ρ^a_{HOMO} is fronter electron density of atom a in the HOMO of molecule A, ρ^b_{LUMO} is fronter electron density of atom b in the LUMO of molecule B; E^a_{HOMO} and E^b_{LUMO} are the orbital energy of the HOMO of molecule A and the LUMO of molecule B; x_a and x_b are the Pauling electronegativity of atom a and b.

Obviously, the more negative of ΔE, the more easily the two molecules A and B react with each other. If there are more than one atom participates in the reaction of molecules A and B in the reactant, the ΔE_i should be calculated respectively and the total ΔE of the reaction should be the sum of each ΔE_i.

In flotation process, when metal sulfides (such as CoS, NiS, FeS, CuS, PbS, HgS and ZnS) contact with MoS_4^{2-} or WO_4^{2-}, the directly interactive atoms are metal atoms(M= Co, Ni, Fe, Cu, Pb, Hg and Zn) in metal sulfides and sulfur or oxygen in molecules MoS_4^{2-} or WO_4^{2-}. In order to simplify the problem, only one interaction of atoms S and O is considered in this work . The ΔE results for the reaction calculated according to Eqn. (1) are shown in Table 3.

Table 3 ΔE of metal sulfides reacting with molecule MoS_4^{2-} or WO_4^{2-}

Metal sulfide	ΔE(MS+ MoS_4^{2-}) / hartree	ΔE(MS+ MO_4^{2-}) / hartree
FeS	- 0.356 73	- 0.062 11
NiS	- 0.338 19	- 0.073 26
CuS	- 0.324 45	- 0.069 24
CoS	- 0.296 02	- 0.056 40
PbS	- 0.262 69	- 0.052 21
HgS	- 0.247 15	- 0.046 73
ZnS	- 0.244 57	- 0.034 55

The ΔE results implies that sulfides are highly reactive towards MoS_4^{2-} but inert with respect to WO_4^{2-}. This is coincident with what we have expected.

5 EXPERIMENT AND REMOVING MOLYBDENUM FROM TUNGSTATE SOLUTION

5.1 Experimental

Series of experiments have been done in laboratory for verifying the efficiency of the potential reagents.

The Na_2WO_4 solution containing 100 g/L WO_3 and 0.6 g/L Mo is acidified to pH= 8.0 with inorganic acid such as HCl or H_2SO_4, and adding a certain amount of Na_2S into it. React at room temperature for 12 h, then sulfide is added into it under stiring condition. After a certain time, the slurry is filtrated to get purified Na_2WO_4 solution.

5.2 Experimetal results

The experimental results are listed in Table 4. Obviously, CoS, NiS and CuS are very effective for incorporating Mo. PbS and FeS are also effective but HgS and ZnS are almost useless. Taking environment and economy factors into consideration, CuS is chosen as the most suitable reagent.

Table 4 Experiment results of removing Mo from Na_2WO_4 solution with new reagent

Metal sulfides	Content of Mo in purified Na_2WO_4 solution/ ($g \cdot L^{-1}$)	Ratio of removing Mo/ %
FeS	0.097	83.8
PbS	0.016	97.3
CoS	0.004	99.3
NiS	0.003	99.5
CuS	0.004	99.3
HgS	0.306	49.0
ZnS	0.400	33.3

Metal sulfides must be active enough.

The ingredient analysis[10] shows that the filter residue by CuS method contains 19% Mo and 1.5% WO_3. CuS shows high selectivity.

6 CONCLUSIONS

1) On ground of difference in microscopic properties of MoS_4^{2-} and WO_4^{2-}, series of sulfides are chosen as new reagent for removing molybdenum from tungstate solution. Theoretical analysis and experimental tests show that CoS, NiS and CuS are all very effective, and CuS is screened out to be the most ideal one.

2) According to the characteristics of this new reagent and the practice of tungsten metallurgy process, a new technique of selectively precipitating molybdenum from tungstate solution can be proposed.

REFERENCES

[1] XU Guang-xian, YUAN Cheng-ye. Solvent Extraction of Terrestrial Rares[M]. Beijing: Science Press, 1987. (in Chinese)

[2] CHEN Zhou-xi, HUANG Shao-ying, ZHOU Liang-yi. Removing molybdenum from tungstate solution by using ion exchange technics[P]. CN Patent: 88105712. 1988.

[3] Blokhin A A, Prekas Y V, Taushkanov V P. Removal of molybdenum from tungstate solution by ionexchange[J]. J Applied Chem, 1989, 5: 985－988.

[4] HUO Guang-sheng, LI Hong-gui, SUN Pei-mei. The application of alkalescent ion exchange resin in the process of removing molybdenum from tungstate solution[J]. Journal of Central South University of Technology, 2000, 31: 30－33. (in Chinese)

[5] JIANG An-ren, JIANG Wei-zhong, PANG Zhen. Removing Mo, As, and P from tungstate solution by using guanidinium-salt[J]. Rare Metal, 1991, 1: 10－12. (in Chinese)

[6] LI Shao-xiu, WANG Xiang-de, ZHANG Xiu-juan. Removing Mo from tungstate solution by using liquid membrane technics [J]. Science and Technology of Membrane, 1996, 16: 33－39. (in Chinese)

[7] GONG Bo-fan, HUANG Wei-zhuang, ZHANG Qi-xiu. The study on counter current cascade extraction process of separation of molybdenum from tungsten with N263[J]. J Central South Institute of Mining and Metallurgy, 1994, 24: 45－48. (in Chinese)

[8] Fukui K, Yonezawa T, Shingu H, et al. A molecular-orbital theory of reactivity in aromatic hydrocarbons[J]. J Chem Phys, 1952, 20: 722－725.

[9] Klopman G. Chemical reactivity and the concept of charge- and frontier-controlled reaction[J]. J Amer Chem Soc, 1968, 90: 223－234.

[10] LI Hong-gui, SUN Pei-mei, LI Yun-jiao, et al. Removal of Mo, As, Sb and Sn from tungstate solution[J]. Trans Nonferrous Met Soci China, 2000, 10(4): 539－541.

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