

THERMODYNAMIC AND STRUCTURAL CHEMISTRY

DISCUSSIONS FOR OXIDATIVE LEACHING OF Cu-Ni SULPHIDE

ORE UNDER ATMOSPHERIC PRESSURE^①

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ABSTRACT HNO₃ was calculated to have much more larger thermodynamical tendency to oxidate copper, nickel and iron sulphides than FeCl₃. The frontline orbits theory also confirmed that NO₃⁻ reacted with nickel and iron sulphides more easily than Fe³⁺. The results of leaching Cu-Ni sulphide ore with FeCl₃ and HNO₃ were theoretically interpreted.

Key words: Cu-Ni sulphide ore leach ferric chloride nitric acid

1 INTRODUCTION

Hydrometallurgy on sulphides had a rapid development in the last two decades. Technologies of hydroleaching copper-nickel sulphides included: bacterial, acidic, ammonia and oxidative leaching, in which the last one was in most common use. The usual oxidants were CuCl₂, O₂, Fe³⁺ [FeCl₃, Fe₂(SO₄)₃], HNO₃, O₃, Cl₂ and so on. Researches on leaching chalcopyrite with Fe³⁺ were in most detail, and satisfactory results had been obtained in chloride solutions because of good complexible characteristics of Cl⁻, large solubility of chlorides, high electric conductivity of solution and easy to electrodeposition of metallic ions in chloride solutions. However it is still difficult for hydrometallurgy to leach directly original sulphide ore under atmospheric pressure, for example, copper-nickel complex sulphide ore, therefore, pressure processes are often used to improve leaching rate and efficiency.

We had investigated the leaching process of copper-nickel original sulphide ore from Xinjiang Province with acidic ferric chloride and nitric acid respectively^[1]. In former situation, the leached fraction about 60% in two stages was not satisfied, even though the ore was pretreated for activation and catalysis, and the hindrance was from passivation of the intermediate product β -NiS in FeCl₃ solution^[2]. Fortunately, HNO₃ succeeded in solving the difficulty, 97.7% of copper and 99.3% of nickel in ore were transferred into solution^[3].

In this paper, difference between the two leaching systems will be discussed in terms of thermodynamics and structural chemistry. The composition of the researched ore is listed in Table 1.

In the original ore, copper and nickel exist in chalcopyrite and pentlandite respectively, and nickel is in the lattice of iron sulphide. Because the ratio of Fe:Ni in the pentlandite is not constant, there are not any thermodynam-

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ic data to be reported about this mineral, so FeS is replaced for following discussion.

2 ANALYSES

Table 2 lists thermodynamical data of some materials and ions in aqueous solution at 25 °C and 100 °C respectively.

Table 3 lists crystal structures, thermo-

dynamical data and other characteristic parameters of some sulphides.

If there is not phase transition in leaching process in the temperature range of 25 ~ 100 °C and Cp keeps constant, $\Delta G_{i,373}^0$ of minerals can be calculated, and results are listed in Table 4 (Leaching in FeCl₃ and HNO₃ solution are both at 90 °C, and data at 100 °C are calculated for the reason of convenience).

Table 1 Composition of copper-nickel sulphide ore (%)

Mineral	Pentlandite	Chalcopyrite	Pyrrhotite	Magnetite	Pyrite	Gangue
Formula	(Ni,Fe) ₉ S ₈	CuFeS ₂	Fe _{1±x} S	Fe ₃ O ₄	FeS ₂	
Content	10.35	13.27	63.92	5.34	1.05	5.95

Table 2 ΔG_i^0 of some components kJ/mol

	S	H ⁺	NO ₃ ⁻	Ni ²⁺	NO	H ₂ O	Fe ³⁺	Fe ²⁺	Cu ²⁺
$\Delta G_{i,298}^0$	-9.5	6.2	-257.2	-3.1	27.5	-306.4	64.3	-35.6	107.0
$\Delta G_{i,373}^0$	-11.7	6.7	-268.0	-7.4	11.4	-312.2	89.4	-24.5	115.2

Table 3 Characteristics of sulphides

Mineral	Pentlandite	Chalcopyrite	Pyrite	Mackinawite	Troilite	Millerite
Formula	(Ni,Fe) ₉ S ₈	CuFeS ₂	FeS ₂	Fe _{1+x} S	FeS	β -NiS
Crystal system	Cubic	Tetragonal	Cubic	Tetragonal	Hexagonal	Hexagonal
Space group	<i>Fm3m</i>	<i>I42d</i>	<i>Pa3</i>	<i>P4/nmm</i>	<i>P62c</i>	<i>R3m</i>
Crystal structure						
<i>a</i> / Å	10.05	5.25	5.42	3.68	5.96	9.62
<i>b</i> / Å	—	—	—	—	—	—
<i>c</i> / Å	—	10.32	—	5.03	11.76	3.15
α / °	—	—	—	—	—	—
β / °	—	—	—	—	—	—
γ / °	—	—	—	—	—	—
Reflectivity (%)	47.0	45.7—50.5	55.0	22—46		53.2—59
Vickers microhardness	202—231	174—219	913—2056	52—58		192—376
Thermal stability/°C	<610	<550	<742	<153	<138	<379
ΔH_f^0 , 298/kJ•mol		-184.8	-171.4		-100.3*	-92.6
ΔG_f^0 , 298/kJ•mol		-185.2	-160.1	-93.2	-100.7	-91.5
S_{298}^0 /J•(mol•K) ⁻¹		124.9	52.9		60.3*	52.9
C_{p298} /J•(mol•K) ⁻¹		69.5	62.1		50.3*	47.1
Magnetic and	Pp.	An.	Di.	Pp.	An.	Pp.
electrical data #	Met.	Semicond.	Semicond.	Met.	Met.	Met.

* NiAs type FeS

Pp. —Pauli paramagnetic; An. —Antiferromagnetic; Di. —Diamagnetic; Met. —Metallic conductor; Semicond.

—Semi conductor

Table 4 $\Delta G_{f, 373}^0$ of some minerals kJ/mol

	(Ni,Fe) ₉ S ₈	CuFeS ₂	FeS ₂	Fe _{1+x} S	FeS	β -NiS
$\Delta G_{f, 373}^0$	-185.8	-160.6			-101.1	-91.9

So, ΔG^0 of main reactions in two leaching solutions at 25 °C and 100 °C are calculated as follows:

	ΔG_{298}^0	ΔG_{373}^0
β -NiS + 2Fe ³⁺		
= Ni ²⁺ + 2Fe ²⁺ + S	-120.9	-155.0
8H ⁺ + 3 β -NiS + 2NO ₃ ⁻		
= 3Ni ²⁺ + 3S + 2NO + 4H ₂ O	-469.1	-525.2
FeS + 2Fe ³⁺		
= 3Fe ²⁺ + S	-144.2	-162.9
4H ⁺ + FeS + NO ₃ ⁻		
= Fe ³⁺ + S + NO + 2H ₂ O	-197.4	-193.0
CuFeS ₂ + 4Fe ³⁺		
= Cu ²⁺ + 5Fe ²⁺ + 2S	-162.0	-202.5
3CuFeS ₂ + 5NO ₃ ⁻ + 20H ⁺		
= 3Cu ²⁺ + 3Fe ³⁺ + 5NO		
+ 6S + 10H ₂ O	-752.0	-758.0
FeS ₂ + 2Fe ³⁺		
= 3Fe ²⁺ + 2S	-94.3	-115.1
4H ⁺ + FeS ₂ + NO ₃ ⁻		
= Fe ³⁺ + S + NO + 2H ₂ O	-138.0	-133.5

There are less differences for each reaction at 25 °C and 100 °C, and temperature affects thermodynamic tendency of leaching reactions at a little degree, but obviously reaction rates, so leaching efficiency increased obviously with temperature up, as shown by experiments.

Comparing above reactions and their ΔG^0 values by equal mole amount of oxidant, oxidative tendencies in HNO₃ solution are much more than those in FeCl₃ to four minerals (β -NiS, FeS, CuFeS₂, FeS₂). Resistance in FeCl₃ leaching comes from passivation of the intermediate product β -NiS, and this hindrance is eliminated in stronger oxidation of HNO₃, so leaching of Cu-Ni sulphide ore with HNO₃ is satisfactory.

From above thermodynamical calculation results, CuFeS₂ is the easiest to be leached, and practical leaching of chalcopyrite with

HNO₃ had 99% leached fraction for Cu by Brenneche^[6], but our experiments just give 85.2% in the first stage leaching, while leached fraction of Ni is 97.3%.

Compared standard electrode potential of sulphides, FeS and α -NiS are very low, and CuFeS₂ is positive relatively.

E^0/V vs. SHE

Fe ²⁺ + S + 2e = FeS	0.0654
Ni ²⁺ + S + 2e = α -NiS	0.1338
Cu ²⁺ + Fe ²⁺ + 2S + 4e = CuFeS ₂	0.4027
Fe ²⁺ + 2S + 2e = FeS ₂	0.4230

The negative nickel sulphide and FeS form galvanic cell with coexisted more positive CuFeS₂ and FeS₂, so resolution of nickel and iron is accelerated and that of copper slowed down. This is the main reason why the leached fraction for copper is not high in the first leaching stage. Then, chalcopyrite comes to be regular just when the negative minerals had consumed, and its leaching is accelerated by pyrite which is of most positive electrode potential. Finally, 97.7% of copper enters solution.

3 DISCUSSIONS ON STRUCTURAL CHEMISTRY

Chalcopyrite has a similar crystal structure with sphalerite, and it is double in volume for a crystal cell, i.e., two copper atoms and two iron atoms replace the original four zinc atoms in the sphalerite. Mackinawite Fe_{1+x}S is a layer structure, an iron atom joints four sulphur atoms equally to be a tetrahedral structure which is different from FeS, and the distance between metallic atoms on the basic plane is short (2.602 Å), but that between metallic layers is longer because of a sandwiched sulphur layer. Pentlandite is of the same structure as Ni₉S₈ or Co₉S₈ (see Fig. 1).

In FeS, Fe²⁺ arranges its electrons in (1s)²(2s)²(2p)⁶(3d)⁶ and the energy levels of 3d, 4s and 4p are closed. Electrons of S²⁻ are arranged in (1s)²(2s)²(2p)⁶(3s)²(3p)⁶. An octahedron is constructed by a Fe²⁺ with its neighbour six S²⁻, in which the valence bond

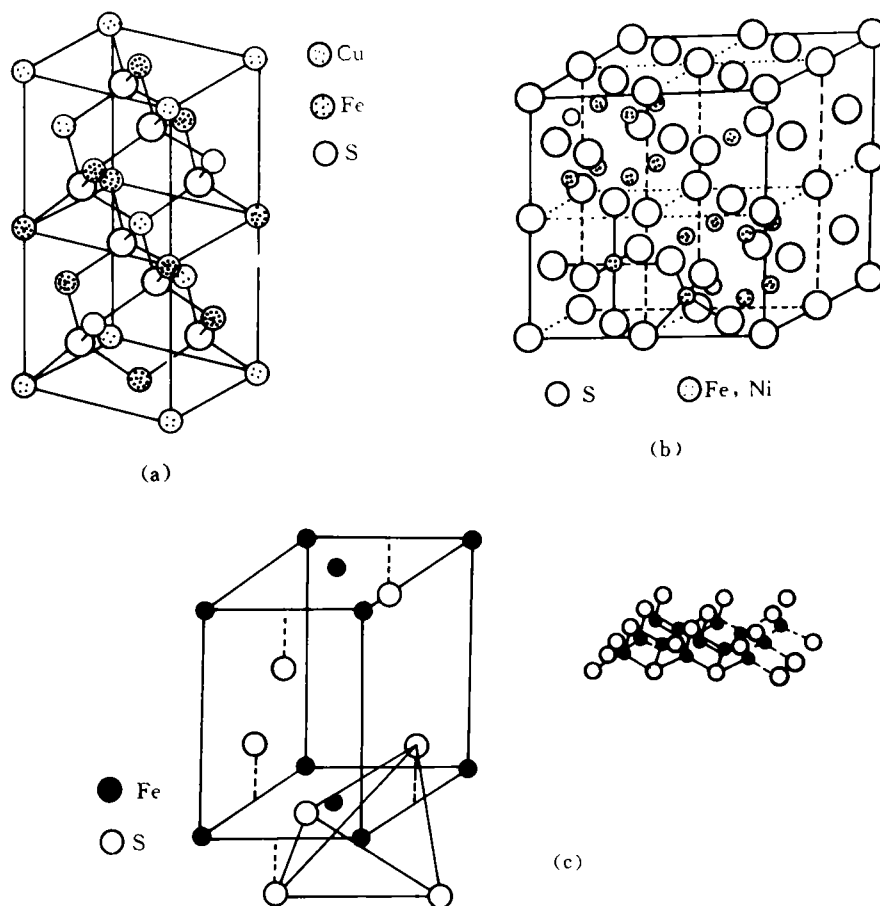


Fig. 1 Schematic crystal structures of CuFeS_2 , $(\text{Ni}, \text{Fe})_9\text{S}_8$, Fe_{1+x}S

(a)— CuFeS_2 ; (b)— $(\text{Ni}, \text{Fe})_9\text{S}_8$; (c)— Fe_{1+x}S

orbitals are re-combined to be new molecular orbitals, including six σ bond orbitals (a_{1g} , t_{1u} , e_g), six σ^* antibond orbitals (e_g^* , a_{1g}^* , t_{1u}^*) and three nonbond ones, as shown in Fig. 2.

Six couples valence electrons of six S^{2-} are filled into six σ molecular orbitals and the d electrons of central ion Fe^{2+} into t_{2g} and e_g^* at the high-spin state because of closed energy level in these two molecular orbitals.

NO_3^- is an inorganic conjugate ion, N atom arranges its electrons in $(1s)^2(2s)^2(2p)^3$, the three atomic orbitals $2s$, $2p_x$ and $2p_y$ are recombined to be equilateral hybridization of sp^2 , and three hybridized orbitals form three σ bond with three p_x atomic orbitals of three oxygen atom respectively, so NO_3^- is plane triangle. Also, $2p_z$ orbital of N atom, with a lone-

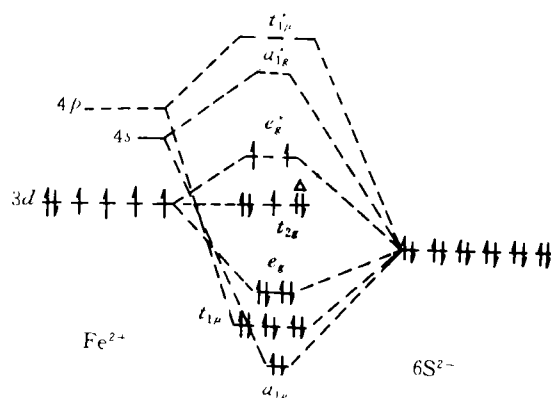
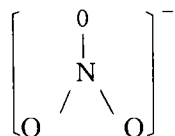


Fig. 2 Schematic diagram for energy level of FeS molecular orbitals

e —doublet degeneracy; t —triplet degeneracy;
 g —central anti-symmetry;

1—symmetrically vertical to the main axis C_2 ;
2—anti-symmetrically vertical to the main axis C_2

pair electrons and verticle to the molecular plane, don't take part in the hybridization, thus, it can form delocalized π bond with three p_z from three oxygen atoms with a single electron for each. So, combining the electrons of NO_3^- , six electrons are occupied in the π bond by four p_z orbits, which is denoted as π_4^6 , and its structural formula is



The frontline orbits theory considers that the highest occupied molecular orbit (HOMO) and the lowest unoccupied molecular orbit (LUMO) of reactants are critical in a chemical reaction, which are named frontline orbits. HOMO and LUMO need the matching symmetry for reaction, and electrons flow from HOMO into LUMO, while the direction should be from lowest electronegative element in one reactant to the highest one in the other reactant.

In FeCl_3 , electrons of Fe^{3+} are arranged in $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^5$, and one of $3d$ orbits is empty and acts as LUMO. In

HNO_3 , the π_4^6 is unsaturated, it is LUMO. While the reductant FeS takes its e_g^* as HOMO. So electrons flow from the e_g^* orbit in FeS to the $3d$ in Fe^{3+} than that of π_4^6 in NO_3^- .

The energy level of e_g^* is closed to that of $3d$, and is higher to π bond in NO_3^- . But N atom has the highest electronegativity of 3.0 while Fe^{3+} is 1.7 and Fe^{2+} 1.8. In FeS structure, the valence electrons are filled in e_g^* and t_{2g} orbits, these two orbits are similar to $3d$ in Fe^{2+} in terms of their energy level and electronic characteristics. So, the valence electrons are easy to flow into the higher electronegative N atom. But the more important factor is the symmetry. Because the e_g^* in FeS contains more components of d_{x^2} and $d_{x^2-y^2}$, their shapes are similar (see Fig. 3).

Therefore, the matching symmetry is satisfied by π in NO_3^- and e_g^* in FeS , but in Fe^{3+} , the requirement is met only when d_{x^2} and $d_{x^2-y^2}$ as LUMO. So NO_3^- can more easily react with FeS and break the crystal structure of copper-nickel sulphide than Fe^{3+} , and good leaching results are reached.

The crystal structure of pentlandite is a mixture of tetrahedron and octahedron (see Fig. 1), in which nickel atoms firstly occupy

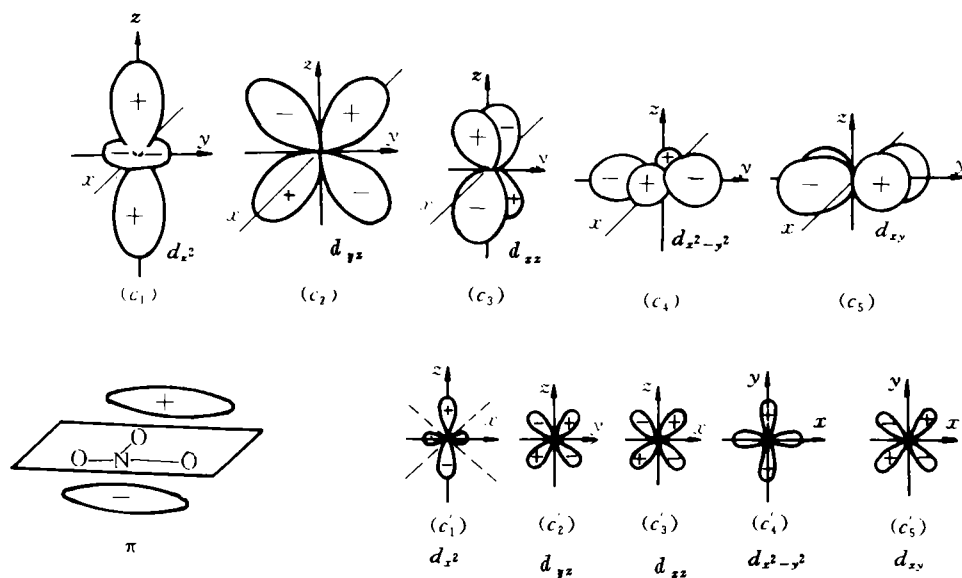


Fig. 3 The angle distribution diagram for d orbits and π orbit (To page 36)

YMg₂, NdMg₂, HoNi₂, YCo₂, NdRu₂ and

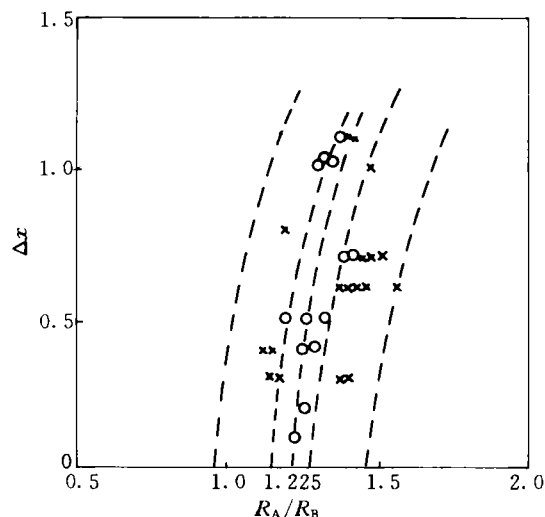


Fig. 3 Melting behaviours of Laves phases formed with two transition metals (Regularities of congruent or incongruent melting)

o—congruent melting; ×—incongruent melting

(From page 33) the central site in the octahedron, and then the others (if there are more to left) accompany with iron atoms to joint with sulphur. Experimental results of electric and magnetic tests show that there are delocalized unpaired electrons in (Ni, Fe)₉S₈, which is similar to character of π_4^* in NO₃⁻, and these two materials have matching symmetry, and closed energy level, so they can react easily.

4 CONCLUSIONS

(1) The calculation results show that HNO₃ has much more larger thermodynamic tendency than FeCl₃ to oxidate copper, nickel and iron sulphides in original ore. HNO₃ can oxidate the intermediate product β -NiS, which resists the further leaching reaction in FeCl₃ solution, so good results can be got with HNO₃.

(2) The reason why the leached fraction of nickel is higher than that of copper is explained with the theory of galvanic cell.

(3) The frontline orbits theory confirms

LaRh₂ are melted incongruently. All these results of prediction have been conformed by experimental results.

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that NO₃⁻ reacts with nickel and iron sulphides more easily than Fe³⁺, so HNO₃ has high leaching efficiency.

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