Production of high purity APT from scheelite and complex tungsten raw material with high Mo content[①]

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Abstract: More than 73% of the tungsten resources in China are scheelite and 41% are high molybdenum content ores, and their dressing becomes increasingly difficult. Such situation calls for new and advanced processes that can treat complex ores and still attain high overall recovery of tungsten. The novel NaOH digestion process and selective precipitation process was developed. The former is universal for leaching tungsten from various tungsten materials, including scheelite concentrate and keeps most of the impurity elements P, As and Si in residue; while the latter is effective for removing impurities such as Mo and Sn. Combined with the traditional ion exchange process, the new process can be used to produce APT that confirms with the Chinese National Standard GB10116-88APT-0 with crystallization ratio of 95%. When treating high molybdenum scheelite concentrate from Shizhuyuan Deposit with WO_3 content of 50% – 55%, recovery of the new process may reach up to about 95% which is grossly the same as that from the traditional way for treating standard wolframite concentrates.

Key words: metallurgy of tungsten; APT with high purity; scheelite

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1 INTRODUCTION

It is reported that more than 75% of APT in China is prepared from standard wolframite concentrate. During 1990's, as the result of consuming wolframite resource, the situation of Chinese tungsten resource has changed as follows[1–3]:

1) Scheelite and/ or scheelite-wolframite deposits have accounted for 73% of the total tungsten resource.

2) Dressing becomes difficult. In the dressing process the recovery of tungsten decreases sharply with the increase of the content of WO_3 in the concentrate obtained. For example, in Shizhuyuan Deposit, when the content of WO_3 in the obtained concentrate increases from 50% to 65%, the recovery of tungsten decreases from 80% to 67%.

3) The content of impurity such as elements Mo, As and Sn in concentrate becomes high. It is reported that more than 41% of the tungsten resource in China is of high molybdenum content, and the ratio of Mo/ WO_3 in concentrate is more than 1.5%.

Under the above situation, we have developed two processes since 1984. The first is novel NaOH digestion process, which is a universal process for leaching tungsten from various raw material(including scheelite concentrate and middlings) with keeping most of the impurities, arsenic, phosphor as well as silicon in residue. The second is a process of selective precipitation of Mo, Sn, As and Sb, which is more effective for removing the above impurities from

tungstate solution.

Combining with the traditional ion exchange process, APT with high purity can be produced from various complex raw material. When treating scheelite concentrate from Shizhuyuan Deposit with a content of 50% – 55% WO_3 and 1.5% Mo, recovery of new process is up to about 95%, which is almost the same as the traditional one for treating standard wolframite concentrate.

2 FLOW SHEET

Fig. 1 shows the flow chart for producing pure APT from scheelite concentrate or complex tungsten raw material.

Tungsten raw materials is digested with NaOH solution. In the digesting process tungsten is leached as Na_2WO_4 and most of the impurities, such as As, P and Si are incorporated inside the residue. The obtained sodium tungstate solution is transformed into $(NH_4)_2WO_4$ by ion-exchange. In the $(NH_4)_2WO_4$ solution obtained, molybdenum as well as part of Sn and As is also remained.

The above impurities are further removed by selective precipitation process with homely developed reagent.

Then super pure APT was crystallized from the purified solution.

The sodium hydroxide digestion process and selective precipitation process are explained as follows.
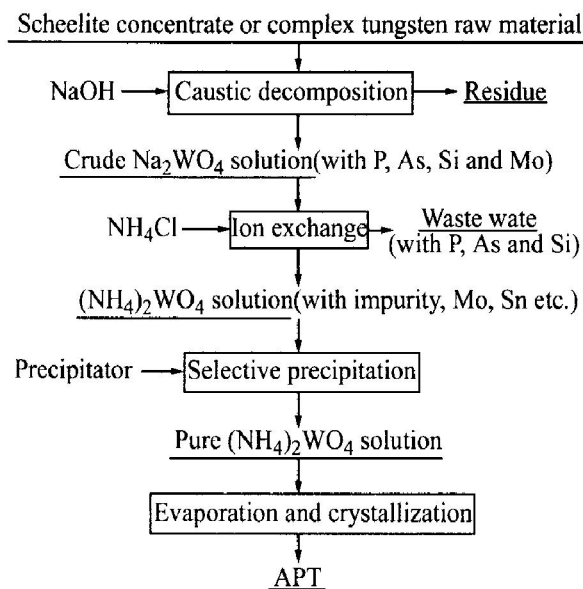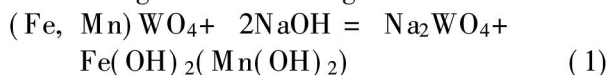
Fig. 1 Flow chart for producing APT from scheelite concentrate and/or complex tungsten raw material

3 NaOH DIGESTION PROCESS

3. 1 Fundamental

In the NaOH digestion process, wolframite is digested according to the following reaction:

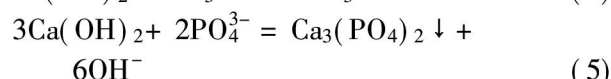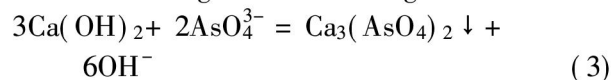$$(Fe, Mn)WO_4 + 2NaOH = Na_2WO_4 + Fe(OH)_2(Mn(OH)_2) \quad (1)$$

As for scheelite, metallurgists[2, 4, 5] considered that it can not be decomposed by NaOH, since the equilibrium constant K for reaction(2) at 25 ℃ is only 2.5×10^{-4}, and it has been proved by the industrial practice that in the NaOH digestion of wolframite concentrate, the recovery of tungsten decreases sharply with the Ca content in the concentrate.

$$CaWO_4 + 2NaOH = Na_2WO_4 + Ca(OH)_2 \quad (2)$$

Since 1980's, we have carried out a series of theoretical research on the reaction of NaOH with scheelite[6]. It has been proved that the apparent equilibrium constant K_C increases with increasing the concentration of NaOH and temperature(K_C is defined as $[Na_2WO_4]/[NaOH]^2$, $[Na_2WO_4]$ and $[NaOH]$ are the equilibrium concentrations of Na_2WO_4 and NaOH, respectively). At 150 ℃ and with NaOH concentration of 4. 06 mol/ L, a K_C value of 2.06×10^{-2} is reached. So in the case of suitable high temperature and NaOH concentration, reaction (2) should be proceed spontaneously.

It has been also proved[7] that impurities As, Si and P, if being leached, will react with $Ca(OH)_2$ from reaction(2) to form insoluble calcium arsenate, calcium silicate and calcium phosphate, and remain in the residue according to the following reactions:

$$3Ca(OH)_2 + 2AsO_4^{3-} = Ca_3(AsO_4)_2 \downarrow + 6OH^- \quad (3)$$

$$Ca(OH)_2 + SiO_3^{2-} = CaSiO_3 \downarrow + 2OH^- \quad (4)$$

$$3Ca(OH)_2 + 2PO_4^{3-} = Ca_3(PO_4)_2 \downarrow + 6OH^- \quad (5)$$

The equilibrium constant of reaction(4) and (5) at 150 ℃ is 1.4×10^{10} and 4.1×10^{11}, respectively and that for reaction(3) at 25 ℃ is 4.8×10^4.

3. 2 Industrial practice

Caustic decomposition is proceeded in specially designed autoclave.

Most sort of concentrates, especially scheelite concentrate and low-grade blended scheelite-wolframite concentrate, can be leached with a high tungsten recovery and low impurity leaching ratio. Some typical results of industrial practice are listed in Table 1.

As listed in Table 1, tungsten recovery of more than 98. 5% is obtained for scheelite concentrate. Even for middling, with 34. 57% WO_3, a high recovery up to 97% still can be got.

The comparison of leaching rate of impurity elements As, P and Si is listed in Table 2. It shows obviously that, in the traditional process more than 50% of As and P can be leached with tungsten, but in present process, it is only 3%-5%.

Even though the content of As, P and Si in

Table 1 Results for decomposition of tungsten concentrate

Concentrate sort	Composition		$x(NaOH)/$ $x(WO_3)$	WO_3 in residue/ %	Recovery of WO_3/ %
	$w(WO_3)/\%$	$w(Ca)/\%$			
Scheelite	67. 65	14. 82	4. 5	3. 10	98. 50
Scheelite	70. 23	15. 84	4. 4	2. 65	98. 60
Blend	64. 70	5. 2	4. 2	2. 03	98. 8
Blend	65. 40	6. 5	4. 3	2. 30	98. 70
Blend	70. 51	3. 42	3. 6	2. 20	99. 03
Middling	34. 57	5. 97	7. 0	1. 60	97. 00

Table 2　Leaching ratio of impurities from different process

Process	Raw material(mass ration)/10^{-2}				Na_2WO_4 solution(mass ratio)/10^{-2}			Impurity leached/%		
	As/WO_3	P/WO_3	Si/WO_3	Ca/WO_3	As/WO_3	P/WO_3	Si/WO_3	As	P	Si
Traditional	0.042	0.032	3.27	0.77	0.024	0.016	0.15	57	50	4.6
Present	2.37	0.36	15.0	17.26	0.069	0.017	0.31	2.9	4.7	2.7

the raw material used in present process is 5 − 10 times of that in traditional one, the quality of the tungstate sodium solution obtained is almost identical.

4　SELECTIVE PRECIPITATION OF Mo, As AND Sn FROM $(NH_4)_2WO_4$ SOLUTION

The $(NH_4)_2WO_4$ solution from ion exchange process still contains Mo, trace Sn and As. In order to remove the above mentioned impurities, many methods were reported, such as precipitation of MoS_3, solvent extraction of thio-molybdate with N_{263}[8], ion-exchange with basic anion resin[9, 10] and ion flotation. But these methods can remove Mo only, and are not suitable for solutions with high impurity content. Based on the investigation on the difference in microscopic properties between WO_4^{2-} and MoS_4^{2-}, AsS_4^{3-}, SnS_3^{2-}, SbS_4^{3-}, it is observed that a complex of sulfite of nonferrous metals can be used as precipitator to remove the above mentioned impurities from tungstate solution effectively[11−14]. At room temperature, the above reagent is added into Mo-bearing solution under stirring condition. Molybdenum as well as Sn and As will combine with it to form precipitate. After filtration, the Mo content in solution can be lowed down to less than 0.01 g/L. Most of As, Sb and Sn can also be removed. Table 3 lists the typical industrial results[15].

Table 3　Results of removing Mo from $(NH_4)_2WO_4$ solution

Initial Mo concentration/ ($g\cdot L^{-1}$)	Mo in purified solution		Mo removed/%
	$c(Mo)/$ ($g\cdot L^{-1}$)	$\dfrac{c(Mo)}{c(WO_3)}$/%	
0.89	0.004	2×10^{-5}	99.5
1.05	0.015	7×10^{-5}	98.5
3.7	0.012	6×10^{-5}	99.7
0.04	0.001	5×10^{-5}	97.5
2.45	0.007	4×10^{-5}	99.7
2.7	0.006	3×10^{-5}	99.4

As seen from Table 3, molybdenum can be depressed to as low as 0.012 g/L even if the initial Mo concentration is high up to 3.70 g/L. This means that about 99.7% of Mo can be removed.

The dry precipitate was assayed to contain 2% − 4% WO_3 and 16% − 18% Mo. It means that the tungsten lost is only 0.15 − 0.22 kg(per 1 kg Mo),

and tungsten recovery up to 99.9% depends on the Mo content in initial $(NH_4)_2WO_4$ solution.

5　QUALITY OF APT

The impurity content of APT crystallized from the purified $(NH_4)_2WO_4$ solution are still lower than that of Chinese National Standard GB-10116-88APT-O when crystallization ratio is controlled as high as 95%.

Table 4 lists the chemical composition of APT produced from tungsten middling (5.5% Ca, 50% WO_3, $w(Mo)/w(WO_3)\approx1\%$, $w(Sn)/w(WO_3)\approx2\%$, $w(As)/w(WO_3)\approx2\%$, $w(Sb)/w(WO_3)\approx0.2\%$) by South-East Tungsten Co. with the present process.

6　APPLICATION IN CHINA

It is noteworthy that the novel process is widely adopted in China. The distribution of the companies is shown in Fig. 2.

Among these 14 factories, account for 45% of the productivity in China adopted the whole process shown in Fig. 1, while other 10 factories adopted half of the flow chart, that is, caustic digestion or selective precipitation process. Al of them account for about 70% of the productivity in China.

Table 4　Chemical composition of APT produced by novel process (Mass fraction, %)

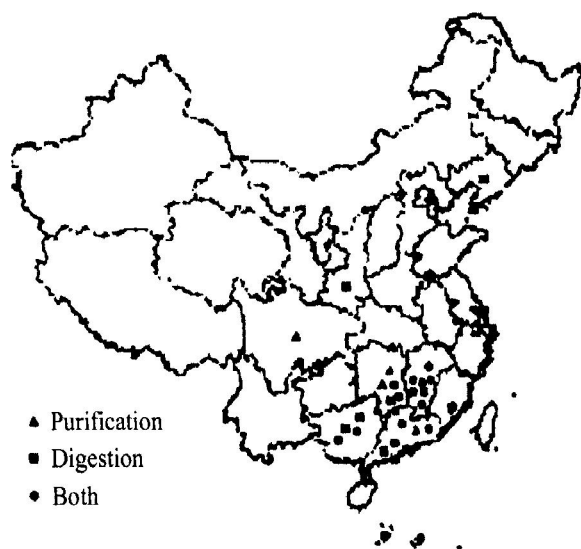| Composition	Raw material	APT
WO_3	50.5	88.5
Ca	6.5	< 0.01
Fe		< 0.01
Mo	0.3 − 0.9	0.0005 − 0.0001
As	0.9 − 1.2	< 0.0001
Sn	0.9 − 1.2	< 0.0001
Sb	0.1	0.005
Mg		< 0.0007
P		< 0.0005
S		0.005
K		< 0.001
Si		< 0.001
Ti, V		< 0.001

Fig. 2 Location of companies adopting novel processes in China

7   CONCLUSIONS

1) NaOH digestion and impurities precipitation process, which deal with the tungsten resource situation of China, are developed. By these methods various tungsten materials with high impurity content can be treated economically to produce APT.

2) These methods are widely adopted in China. More than half of the productivity are produced by these methods.

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