Thermodynamics for Leaching of Scheelite—Pseudo-Ternary-System Phase Diagram and Its Application

ZHONGWEI ZHAO and HONGGUI LI

For thermodynamic reasons, it has been considered that NaOH cannot be used for the digestion of scheelite. Though the caustic thermal mill process has been applied in industry for a long time, people still do not understand it well. In this article, a method called the "pseudo-ternary-system diagram method" is proposed and is used as a tool for carrying out thermodynamic analysis of the NaOH digestion of scheelite. A theoretical explanation is also provided for the concentration effect of Na_2CO_3 on scheelite digestion.

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I. PROPOSAL OF PROBLEM

THE NaOH digestion was once only considered to treat high-quality wolframite. Even less than 1 wt pct of the calcic content in the raw materials caused the digestion rate to decrease dramatically. The thermodynamic calculation shows that its reaction equilibrium constant is only 2.5×10^{-4} at 25 °C.

$$CaWO_{4(s)} + 2NaOH_{(aq)} = Na_2WO_{4(aq)} + Ca(OH)_{2(s)} \quad [1]$$

Based on this and some unsuccessful experiences digesting scheelite with NaOH, many experts thought scheelite could not be digested with NaOH in industrial conditions.[1,2]

In the 1980s, Honggui Li *et al.*[3] developed the caustic thermomilling process. In this technology, NaOH was used as the leaching agent to digest tungsten ores in a heat ball-mill reactor. The technology possessed a wide applicability and could not only digest the wolframite concentrate, but also the wolframite and scheelite blend concentrate, and even the scheelite concentrate and the scheelite tailing. The technology was widely popularized at home and earned the second prize of State Technological Invention Award due to its outstanding advantages.

This novel technology positively discarded the old prejudices. However, this kind of "abnormity" brought some theoretic puzzles too: How could this reaction with such a low equilibrium constant can be achieved so completely? Therefore, the equilibrium constants of Reaction [1] were measured systematically. The equilibrium constants are as given in Table I.[4,5]

From Table I, it is clear that K_a increased with increasing temperature. The temperature of the heat ball-mill reactor is 160 °C, which indicated that the change rule of K_a is beneficial to the novel technology. However, the value of the equilibrium constant, actually yet very small, cannot make the reaction proceed in the correct direction, let alone completely (generally, the leaching rate of the thermomiller is greater than 97 pct, even more than 99 pct).

The thermomiller made use of the enhancive effect of mechanical activation on chemical kinetics. The research shows that this kind of effect can greatly enhance the reaction velocity. Does the mechanochemical effect cause this kind of "abnormity"? According to the theory of mechanochemistry, the ball-mill action could enhance the chemical potential of scheelite, which was proved by a large amount of theoretical research. The authors supposed scheelite suffered intense mechanical action during the process of ball milling and leaching; its Gibbs free energy inclined to increase to a greater extent and became more positive. Thereby, the Gibbs free energy of Reaction [1] could become negative, which could make the reaction proceed.[6,7] However, later we realized that the hypothesis, active $CaWO_4$ coexisted with a heavier concentration Na_2WO_4, actually was impossible. Compared with the stable structure, namely, inactive $CaWO_4$, such a heavy concentration of Na_2WO_4 solution was apparently supersaturation. The stable structural $CaWO_4$ could be precipitated spontaneously from solution.

Therefore, there were some theoretic problems regarding digesting scheelite with the caustic decomposing thermomiller. New theories and methods are required to resolve the problem.

II. REFERENCING FROM ALLIED DISCIPLINE

Considering this problem, we noticed the significant light metal metallurgical technology, which leaches bauxite with the Bayer process.[8] The Bayer process was invented 100 years ago and was widely used in aluminum smelting plants around the world. No one doubted its feasibility of thermodynamics yet. The reaction of treating bauxite with NaOH is as follows:

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Table I. Reaction Equilibrium Constants of $CaWO_{4(s)}$ with $NaOH_{(aq)}$

Temperature (°C)	70	90	130	150
Equilibrium constant	1.00×10^{-4}	1.8×10^{-3}	6.00×10^{-3}	10.5×10^{-3}

Table II. Equilibrium Constant of Reaction [2]

Temperature (°C)	25	30	45	60	80	100	120
Equilibrium constant	0.01	0.04	0.15	0.27	0.34	0.51	0.53

$$Al_2O_3 \cdot xH_2O + 2NaOH + aq \rightleftharpoons 2NaAl(OH)_4 + aq \qquad [2]$$

In the former Soviet Union during the 1950s, the equilibrium constants of Reaction [2] were determined, and the results are shown in Table II.[9]

Comparing Reactions [1] and [2], we find some similarities: both of them used NaOH as the leaching agent and both had a smaller equilibrium constant. Of course, there were some differences as well: some solid products were formed in the reaction of digesting scheelite, while no solid product was found in Reaction [2]. Why did researchers not think there were some "abnormalities" in the process of leaching bauxite with the Bayer process?

We again noticed that the equilibrium constant, at present, has not been adopted actually in the textbooks and the research literature of aluminum metallurgy, but the ternary system phase diagram of Na_2O-Al_2O_3-H_2O (Figure 1) was used as a tool for thermodynamics analysis. Two basic principles of Bayer process are as follow:

(1) Upon the conditions of adding seed and constant agitation, the sodium aluminate solution formed in the process of leaching bauxite with NaOH can precipitate the aluminum hydroxide.
(2) After decomposing, spent liquid can be used to leach a new batch of bauxite at high temperatures by evaporating crystallization.

Making use of the two processes alternately, batches of bauxite were digested to obtain the aluminum hydroxide. This is what is called the Bayer process. The essential part of the Bayer process is that Reaction [2] proceeds in different directions on different conditions.

From Figure 1, at any temperature, increasing the temperature and the concentration of Na_2O were beneficial to increasing the equilibrium concentration of Al_2O_3. Under some conditions, the equilibrium concentration could reach 20 pct, or even close to 40 pct. So, apparently, it was not a problem for leaching bauxite.

Is it possible that an analogous equilibrium phase diagram used as the theoretic tool can be described for the NaOH digestion of scheelite? Referencing the thermodynamic analysis method of alumina, the abnormal phenomena of tungsten hydrometallurgy could be explained, but it was different from the Bayer process. When scheelite was digested, an additional product, $Ca(OH)_2$, formed. At that time, the system became four component. At first view, the equilibrium of the system could not be illustrated with a simple ternary system equilibrium phase diagram.

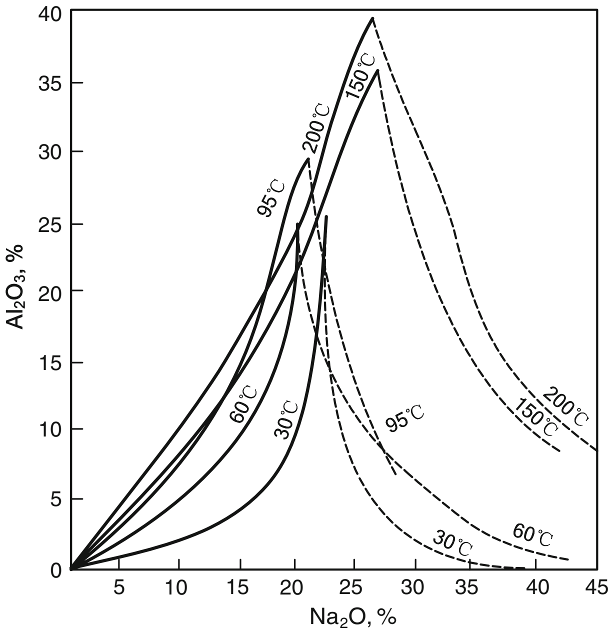

Fig. 1—Equilibrium phase diagram of Na_2O-Al_2O_3-H_2O.

III. PSEUDO-TERNARY SYSTEM PHASE DIAGRAM OF DIGESTING TUNGSTEN

$Ca(OH)_2$ was a kind of compound with relatively less solubility, and its solubility became smaller in the NaOH solution. Considering the equilibrium relation of the aqueous solution system, we could ignore the relatively small amount of solubilized $Ca(OH)_2$ and regard the solution system as a ternary system composed of Na_2O-WO_3-H_2O. Therefore, the equilibrium phase diagram could be described.

The literature[10] showed the solubility value of Na_2WO_4 at different temperatures in the aqueous solution. The literature[4] showed the tungsten concentration balanced with scheelite at different temperatures and NaOH concentrations. Based on the data of the literature referenced,[11] the relation between the solution density with NaOH and Na_2WO_4 concentrations, the mass percent of Na_2O, WO_3, and H_2O could be determined in equilibrium. Figure 2 can be obtained by imitating Figure 1.

Figures 1 and 2 are extremely analogous. In Figure 1, the equilibriums are all composed of two arc lines that form a figure "∧" with hemline at different temperatures. The location of this figure changed little with

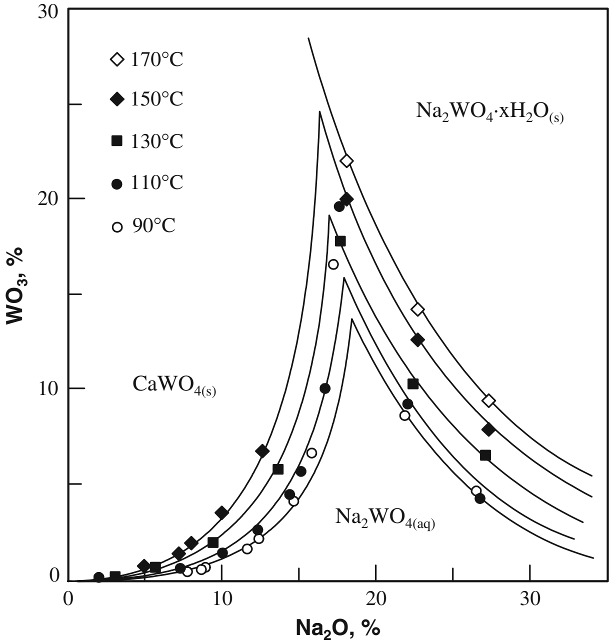

Fig. 2—Equilibrium phase diagram of (CaO-)Na_2O-WO_3-H_2O.

temperature, but its height rose with the increasing temperature in the main. The left arc line of the figure represents the equilibrium between the alumina hydrate solid and the sodium aluminate solution; alumina hydrate could exist steadily on or above the line. However, on the right arc line, the equilibriums were established between the solution and solid crystal of sodium aluminate. In other words, alumina hydrate becomes unstable thermodynamically. At the cross-point of the two arc lines, alumina hydrate (or bauxite) and sodium aluminate (or sodium aluminate hydrate) coexist in the thermodynamic equilibrium.

Analogously, in Figure 2, the equilibriums were all composed of two arc lines, which also formed a figure "∧" with hemline at different temperatures. The location of the figure changed little with temperature, but its height also rose with the increasing temperature in the main. However, the left arc line of the figure represents the equilibrium between the scheelite solid and sodium tungstate solution; the scheelite could exist steadily. On the right arc line, the equilibriums were established between the solution and solid crystal of sodium tungstate. In other words, scheelite becomes unstable thermodynamically. At the cross-point of the two arc lines, scheelite and sodium tungstate (or sodium tungstate hydrate) coexist in the thermodynamic equilibrium.

Because the solubility of CaO was ignored, the phase diagram was not a real triple system. Therefore, it could be called a pseudo-ternary-system phase diagram.

IV. APPLICATION IN TUNGSTEN METALLURGY

From Figure 2, many questions about NaOH digestion of tungsten ore could be understood more easily.

Table III. Influence of Temperature to the Leaching Rate of Megabasite and Scheelite Bulk Concentrate

Temperature (°C)	100	110	120	130	150
Leaching rate (pct)	81.75	81.48	87.62	90.02	98.73

Note: the grade is 31.84 pct, the content of CaO is 4.36 pct, the dosage of NaOH is 3 times the theoretical dosage, the ratio of solid to solution is 1:1, and the leaching time is 3 h.

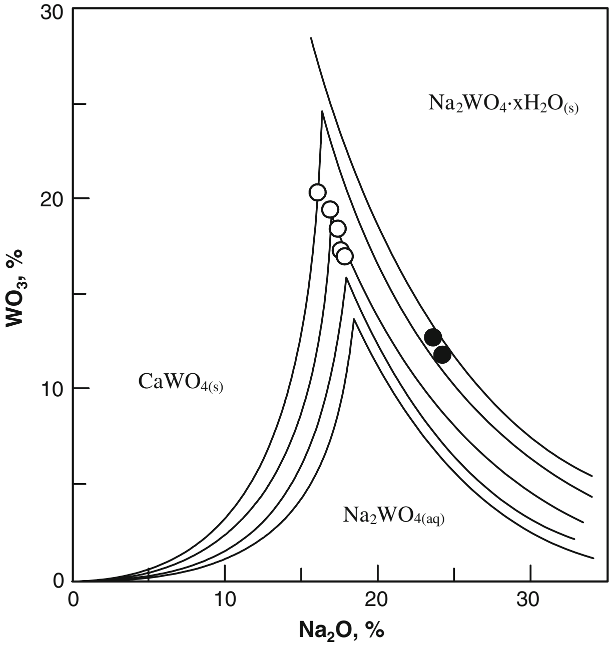

Fig. 3—Pseudo-ternary-system phase diagram for analyzing the data of Tables III and IV.

Some literature[12] reported the leaching rate of a kind of tungsten ore; its results are shown in Table III.

According to our practice, the leaching rate no longer had a distinct change after less than 1 hour during the leaching process of the thermomiller, which showed the reaction had basically reached equilibrium. So the leaching datum of Table III could be regarded as equilibrium data, which did not cause too great a deviation. Drawing these data on the pseudo-ternary-system phase diagram by means of a hollow dot, Figure 3 could be obtained.

From Figure 3, when the equilibrium concentration of Na_2O did not exceed the top cross-point of "∧," the reachable concentration of WO_3 in equilibrium actually decided the leaching rate. This was the reason why the leaching rate increased with the increasing temperature in Table III. However, some experiments indicated that the temperature did not have a great influence on digestion, as shown in Table IV, which seems to be incompatible with Table III.

When the datum of Table IV was described in Figure 3, its location distribution was mainly on the solid dot. In order to identify this clearly, only two data points were described. It is interesting that these dots

Table IV. Influence of Temperature to the Leaching Rate of Scheelite Bulk Concentrate

Temperature (°C)	154	156	155	170	180
Leaching rate (pct)	99.03	98.85	99.39	98.33	98.67

Note: the grade is 72.23 pct, the content of CaO is 15.84 pct, the dosage of NaOH is 2.20 to 2.37 times the theoretical dosage, and the leaching time is 70 to 90 min.

located on the right arc of "∧"; the system was in equilibrium between the solution and crystal of sodium tungstate, and scheelite already became unstable. So, scheelite will be leached under the huge thermodynamics impetus and become solubilized sodium tungstate. Correspondingly, the solution becomes supersaturated, and sodium tungstate crystal was precipitated constantly until scheelite disappeared completely. From Figure 3, regardless of how high or low the temperature, the phenomenon was the same. Therefore, scheelite could be digested completely in spite of the highness or lowness of temperature as long as the reaction time was sufficiently long; this phenomenon of the lack of influence of temperature on leaching rate in shown in Table IV as well.

From this, using the pseudo-ternary-system phase diagram not only could well explain the NaOH digestion of scheelite, but could also provide the reasonable theoretical proof for the experimental phenomenon that seems incompatible. It is also easy to determine the diagram that can predict the leaching effect on a certain condition or choose an appropriate leaching condition for some raw material.

Using the pseudo-ternary-system phase diagram can analyse the similar research problem. For example, the NaOH digestion of scheelite was studied under the condition of electric field action.[13] Because of the low ratio of solution to solid, the Na_2O concentration of the system must be very high. In Figure 4, the leaching equilibrium located on the further right of "∧," which ensured great impetus in thermodynamics. Just under this condition, the solution viscosity was very large, which consequently influenced the diffusion of NaOH and the leaching velocity. However, after introducing the alternative electric field, NaOH was compelled to transfer impetuously and so conquered the negative influence of big viscosity, and tungsten was digested successfully.

The pseudo-ternary-system phase diagram can make the theoretical analysis of other tungsten leaching systems or other metal leaching processes. Taking the example of sodium carbonate digestion of scheelite, its reaction is as follows:

$$CaWO_{4(s)} + 2Na_2CO_{3(aq)} = Na_2WO_{4(aq)} + CaCO_{3(s)} \quad [3]$$

It was found that the exorbitant initial concentration of sodium carbonate was harmful to leaching. Soviet scholars even pointed that when the concentration of sodium carbonate exceeded 230 g/L, the rate of recovery would decrease sharply, which has been proved by many researchers.[14] There are many reasons for this finding. The relatively uniform explanations are that the excessive concentration sodium carbonate reacted with calcium carbonate to produce $Na_2CO_3{\cdot}CaCO_{3(s)}$ or $Na_2CO_3{\cdot}2CaCO_{3(s)}$, so the leaching agent, sodium carbonate, was consumed.[12] However, according to the research of the AMAX Corporation, when the concentration of sodium carbonate was 360 g/L, only 1 pct Na was analyzed in the leaching residue, so these double-salts were decomposed during the process of washing. According to the literature, it took 10 to 12 hours to produce this kind of double-salt at 100 °C; it seemed that these double-salts were hard to produce and easy to decompose. Then what caused the decrease of leaching rate on the condition of excessive concentration sodium carbonate?

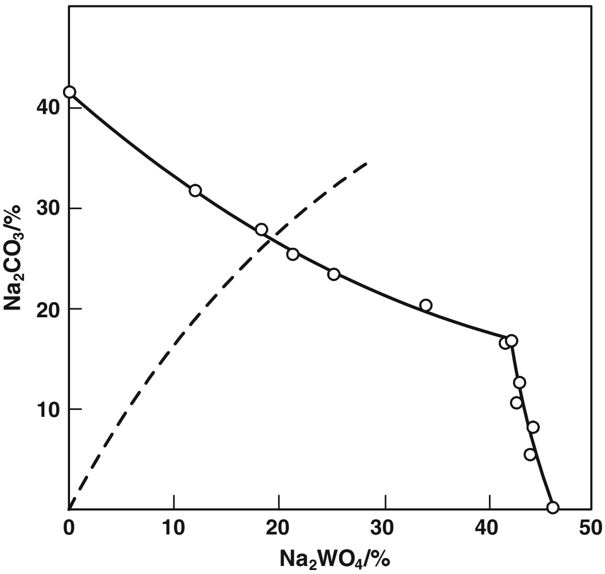

Fig. 4—Pseudo-ternary-system phase diagram of the sodium carbonate digestion of scheelite.

The literature[15] gave the equilibrium phase diagram of Na_2CO_3-Na_2WO_4-H_2O, which is shown on the solid line of Figure 4. An inflexion point was on the solid line. It is the dissolving equilibrium line of sodium carbonate over the inflexion point, while it is the dissolving equilibrium line of sodium tungstate below the inflexion point. Based on this, the pseudo-ternary-system phase diagram of Na_2CO_3 digestion of scheelite can be described.

The solubility of calcium carbonate is also so small that it can be ignored. The equilibrium line of Reaction [3] could be described grossly according to the experimental datum from the literature.[14] It was shown as the dashed line in Figure 4. Figure 4 also includes a figure of "∧." The figure located on the *Y*-axis is due to the different choice of coordinate axis, but it did not influence the analysis.

Comparing Figures 2 and 4, the dashed line in Figure 4 is the same as the right arc line in Figure 2; they are both the leaching equilibrium lines of $CaWO_4$.

On these lines, the concentration of tungsten would increase correspondingly by increasing the concentration of Na_2CO_3 or NaOH, which was beneficial to leaching.

However, the property of another half line was different in the two figures, one was the dissolving equilibrium line of leaching agent Na_2CO_3 (Figure 4), while the other was the dissolving equilibrium line of product Na_2WO_4 (Figure 2). If the concentration of Na_2CO_3 was high, then the value corresponding to the top cross-point of "∧" in Figure 4, the concentration of Na_2WO_4, would increase until it reached the solid line. In order to prove this, suppose a small amount of Na_2WO_4 was added to the solution system, and it could cause an increase in Na_2WO_4 concentration, which made the composition point of the system exceed the saturated equilibrium line of Na_2CO_3 and inevitably cause the precipitation of Na_2CO_3 from the supersaturated solution. The decreasing concentration of the leaching agent, Na_2CO_3, in reverse can cause Reaction [3] to proceed toward the left direction, which made Na_2WO_4 transfer back into scheelite and caused the decrease in concentration. Just for this, the excessive concentration of Na_2CO_3 is harmful for leaching. This is just contrary to that of NaOH digestion, supposing when the concentration of the leaching agent NaOH was higher than the top cross-point of "∧" in Figure 2; then, once the concentration of Na_2WO_4 increased a little, this part of Na_2WO_4, but not the leaching reagent NaOH, crystallized out from the solution.

V. CONCLUSIONS

1. The method of the pseudo-ternary-system phase diagram is brought forward, and the thermodynamic equilibrium diagram was described for the NaOH digestion of scheelite.
2. Making use of the pseudo-ternary-system phase diagram, NaOH digestion of scheelite is explained reasonably in thermodynamic.
3. Making use of the pseudo-ternary-system phase diagram, the thermodynamic reason of concentration effect is analyzed for the process of Na_2CO_3 digestion of scheelite.

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