

Thermodynamic analysis on sodium carbonate decomposition of calcium molybdenum

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Abstract: According to the principle of mass balances and thermodynamic data, $\lg [\text{Me}]$ —pH diagrams ($\text{Me}=\text{Ca}, \text{Mo}$) for Ca-Mo- CO_3 - H_2O system at 25 °C were presented with total dissolved carbon-containing ions concentrations of 0.01 mol/L and 1 mol/L, and $\lg [\text{Me}]$ —pH diagram for Ca-Mo- H_2O system at 25 °C was also depicted. The effects of system pH value and total dissolved carbon-containing ions concentrations on the concentrations of the species in Ca-Mo- CO_3 - H_2O system were studied. The results show that the stability region of CaMoO_4 reduces significantly in the presence of sodium carbonate. In order to achieve effective leaching of molybdenum from CaMoO_4 , a certain concentration of sodium carbonate is necessary. High total dissolved carbon-containing ions concentrations and high pH values facilitate to the leaching of CaMoO_4 and dissolved sodium carbonate is an efficient leaching agent for decomposing CaMoO_4 .

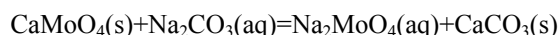
Key words: calcium molybdenum(CaMoO_4); sodium carbonate; decomposition; thermodynamic analysis; concentration logarithm diagram

1 Introduction

Calcium molybdenum(CaMoO_4) mainly exists in seyrigite, molybdenum residue of ammonia-leaching, low-grade concomitancy ore with complexity composition and multi-metal after roasted and spent catalyst with molybdenum, etc. Because of lacking deep study on thermodynamic characteristics in this system, it is difficult to locate the species that play a role in the leaching process with dissolved sodium carbonate. The optimum leaching conditions for decomposing CaMoO_4 are usually determined by experiments[1–6].

Since the principle of potential—pH (E —pH) diagrams was created by POURBAIX[7], the diagrams have played a very important role in many fields and are widely used[8–15]. OSSEO-ASARE[16] presented E —pH diagram of Ca-Mo- CO_3 - H_2O system at 25 °C ($[\text{Mo}]=[\text{Ca}]=10^{-3}$ mol/L) for molybdenum leaching. The diagram shows that E —pH predominance area for equilibrium involves Ca^{2+} , CaMoO_4 , $\text{Ca}(\text{OH})_2$, $\text{Ca}(\text{OH})^+$ and a large CaMoO_4 stability field in high pH region. As a matter of fact, the overall reactions for the decomposition of CaMoO_4 by dissolved sodium

carbonate may be represented as[4]



It can be seen that the reaction is a double decomposition reaction rather than an oxidation-reduction reaction. In the multi-species system, the practical application of E —pH diagram has its limitation in analyzing the Ca-Mo- CO_3 - H_2O system. In order to judge the conditions under that better results can be obtained, it is often necessary to know how the solution components influence the solubility of poorly soluble mineral by means of concentration logarithm diagrams[17], which is a predictive and analytical tool in hydrometallurgical process. So the concentration logarithm diagram can be used to analyze the carbonate decomposition process. In this paper, a simple and convenient calculation method was introduced according to mass balance principle. Calculations were made to express equilibrium relations among associated aqueous species in terms of total concentrations rather than the individual dissolved species to establish $\lg [\text{Me}]$ —pH diagrams in Ca-Mo- CO_3 - H_2O system at 25 °C. The effects of pH value and total dissolved carbon-containing ions concentration on the equilibrium in Ca-Mo- CO_3 - H_2O

systems were also analyzed.

2 Calculation of concentration logarithm diagrams

2.1 Reactions in aqueous solution and thermodynamic data

Table 1 lists reactions in aqueous solution and a summary of thermodynamic data in Ca-Mo-CO₃-H₂O and Ca-Mo-H₂O systems at 25 °C.

Table 1 Reactions in aqueous solutions and selected equilibrium constants for systems of Ca-Mo-CO₃-H₂O and Ca-Mo-H₂O at 25 °C [16, 18]

No.	Reaction	lg K
1	$\text{CaMoO}_4(\text{s}) = \text{Ca}^{2+} + \text{MoO}_4^{2-}$	-8.53
2	$\text{CaCO}_3(\text{s}) + 2\text{H}^+ = \text{Ca}^{2+} + \text{H}_2\text{CO}_3$	8.28
3	$\text{CaCO}_3(\text{aq}) = \text{Ca}^{2+} + \text{CO}_3^{2-}$	-3.15
4	$\text{Ca}(\text{HCO}_3)^+ = \text{Ca}^{2+} + \text{CO}_3^{2-} + \text{H}^+$	-11.33
5	$\text{H}_2\text{CO}_3(\text{aq}) = \text{HCO}_3^- + \text{H}^+$	-6.35
6	$\text{HCO}_3^- = \text{CO}_3^{2-} + \text{H}^+$	-10.33
7	$\text{Ca}^{2+} + \text{OH}^- = \text{Ca}(\text{OH})^+$	1.40
8	$\text{Ca}^{2+} + 2\text{OH}^- = \text{Ca}(\text{OH})_2(\text{aq})$	2.77
9	$\text{Ca}(\text{OH})_2(\text{s}) = \text{Ca}^{2+} + 2\text{OH}^-$	-5.22
10	$\text{H}_2\text{MoO}_4(\text{s}) = \text{MoO}_4^{2-} + 2\text{H}^+$	-18.84
11	$\text{H}_2\text{MoO}_4(\text{aq}) = \text{MoO}_4^{2-} + 2\text{H}^+$	-6.85
12	$\text{HMoO}_4^- = \text{MoO}_4^{2-} + \text{H}^+$	-5.01
13	$\text{MoO}_2^{2+} + 2\text{H}_2\text{O} = \text{MoO}_4^{2-} + 4\text{H}^+$	-8.33
14	$\text{MoO}_2(\text{OH})^+ + \text{H}_2\text{O} = \text{MoO}_4^{2-} + 3\text{H}^+$	-7.88

The equilibria of total dissolved molybdenum-containing ions concentration, total dissolved calcium-containing ions concentration and total dissolved carbon-containing ions concentrations were respectively established according to the equilibrium equations in Ca-Mo-CO₃-H₂O system and the principle of mass balance.

2.2 Calculation method

1) Based on reactions in aqueous solution and selected equilibrium constants of equations No.10 to 14 in Table 1, the species of MoO_4^{2-} , HMoO_4^- , $\text{MoO}_2(\text{OH})^+$, MoO_2^{2+} and $\text{H}_2\text{MoO}_4(\text{aq})$ exist in Ca-Mo-CO₃-H₂O system. The mass balance for total soluble Mo is given by

$$[\text{Mo}]_{\text{T}} = [\text{MoO}_4^{2-}] + [\text{HMoO}_4^-] + [\text{MoO}_2(\text{OH})^+] + [\text{MoO}_2^{2+}] + [\text{H}_2\text{MoO}_4(\text{aq})]$$

There exist

$$[\text{H}_2\text{MoO}_4(\text{aq})] = \exp(6.85 - 2\text{pH}) \cdot [\text{MoO}_4^{2-}]$$

$$[\text{HMoO}_4^-] = \exp(5.01 - \text{pH}) \cdot [\text{MoO}_4^{2-}]$$

$$[\text{MoO}_2^{2+}] = \exp(8.33 - 4\text{pH}) \cdot [\text{MoO}_4^{2-}]$$

$$[\text{MoO}_2(\text{OH})^+] = \exp(7.88 - 3\text{pH}) \cdot [\text{MoO}_4^{2-}]$$

2) From equations No.1 to 4 and equations No.7 to 9 in Table 1, the species of Ca^{2+} , $\text{Ca}(\text{OH})^+$, $\text{Ca}(\text{OH})_2(\text{aq})$, $\text{Ca}(\text{HCO}_3)^+$ and $\text{CaCO}_3(\text{aq})$ exist in the system. The mass balance for total soluble Ca is given by

$$[\text{Ca}]_{\text{T}} = [\text{Ca}^{2+}] + [\text{Ca}(\text{OH})^+] + [\text{Ca}(\text{OH})_2(\text{aq})] + [\text{Ca}(\text{HCO}_3)^+] + [\text{CaCO}_3(\text{aq})]$$

There exist

$$[\text{Ca}(\text{OH})_2(\text{aq})] = \exp(2\text{pH} - 25.23) \cdot [\text{Ca}^{2+}]$$

$$[\text{Ca}(\text{OH})^+] = \exp(\text{pH} - 12.6) \cdot [\text{Ca}^{2+}]$$

$$[\text{Ca}(\text{HCO}_3)^+] = \exp(11.33 - \text{pH}) \cdot [\text{CO}_3^{2-}] [\text{Ca}^{2+}]$$

$$[\text{CaCO}_3(\text{aq})] = 10^{3.15} \cdot [\text{CO}_3^{2-}] [\text{Ca}^{2+}]$$

3) From equations No.2 to 6 in Table 1, there are species of $\text{H}_2\text{CO}_3(\text{aq})$, CO_3^{2-} , $\text{Ca}(\text{HCO}_3)^+$, HCO_3^- and $\text{CaCO}_3(\text{aq})$ in the system. The mass balance for total soluble C is given by

$$[\text{C}]_{\text{T}} = [\text{H}_2\text{CO}_3(\text{aq})] + [\text{CO}_3^{2-}] + [\text{Ca}(\text{HCO}_3)^+] + [\text{HCO}_3^-] + [\text{CaCO}_3(\text{aq})]$$

There exist

$$[\text{Ca}(\text{HCO}_3)^+] = \exp(11.33 - \text{pH}) \cdot [\text{CO}_3^{2-}] [\text{Ca}^{2+}]$$

$$[\text{HCO}_3^-] = \exp(10.33 - \text{pH}) \cdot [\text{CO}_3^{2-}]$$

$$[\text{H}_2\text{CO}_3(\text{aq})] = \exp(16.88 - 2\text{pH}) \cdot [\text{CO}_3^{2-}]$$

$$[\text{CaCO}_3(\text{aq})] = 10^{3.15} \cdot [\text{CO}_3^{2-}] [\text{Ca}^{2+}]$$

4) When pH value is low, the H_2MoO_4 precipitation will be formed. According to equations No.10 and 11, there exists

$$[\text{H}_2\text{MoO}_4(\text{aq})] = 10^{-11.99} \text{ mol/L}$$

5) In CaMoO_4 stability region, there exists

$$[\text{Ca}]_{\text{T}} = [\text{Mo}]_{\text{T}}$$

6) When pH value increases, CaCO_3 precipitation will be formed. According to equations No.2 and 3, there exists

$$[\text{CaCO}_3(\text{aq})] = 10^{11.43} \text{ mol/L}$$

7) When pH value is high, the $\text{Ca}(\text{OH})_2$ precipitation will be formed. According to equations No.8 and 9, there exists

$[\text{Ca}(\text{OH})_2(\text{aq})]=10^{-2.45} \text{ mol/L}$

Other variables can be obtained from equations in Table 1 by the established simultaneous equations system under given condition.

The determination of stability depends on the availability of relevant equilibrium constants and a variety of soluble ions concentrations that are known to exist[16]. However, there are insufficient data on ion activity coefficient, and so are the ones on temperature effects. The approach taken in this paper is limited at 25 °C and ion activity is replaced by ion concentration in calculation.

3 Results and discussion

3.1 Ca-Mo-H₂O system

Fig.1 shows the $\lg[\text{Me}]$ —pH diagram for Ca-Mo-H₂O system at 25 °C, which indicates that the Ca-Mo-H₂O system is dominated by large CaMoO_4 stability field between pH 7.3 and pH 14.5. The location of stability field matches the E —pH diagram presented by OSSEO-ASARE[14]. Ca^{2+} concentration and MoO_4^{2-} concentration are almost constant in this stability field.

When pH value is less than 7.3, MoO_4^{2-} exists in the form of HMoO_4^- and H_2MoO_4 precipitations. Meanwhile, the free MoO_4^{2-} concentration decreases. Because the solubility product constant of CaMoO_4 is unchangeable, the free Ca^{2+} concentration increases, and the concentration of other species that relate with the concentration of MoO_4^{2-} and Ca^{2+} change. As a matter of fact, CaMoO_4 would be decomposed by acid under this condition.

With the increase of pH value, Ca^{2+} exists in the form of $\text{Ca}(\text{OH})^+$ complex, and the free Ca^{2+} concentration decreases; while the concentration of MoO_4^{2-} increases because of unchanged solubility product constant.

When pH value is higher than 14.5, the Ca^{2+} turns into $\text{Ca}(\text{OH})_2$ precipitation with the increase of alkalinity in Ca-Mo-H₂O system and the free Ca^{2+} concentration decreases. Under this condition, it is facilitating to the increasing concentration of the free MoO_4^{2-} .

3.2 Ca-Mo-CO₃-H₂O system

Fig.2 shows the $\lg[\text{Me}]$ —pH diagram for Ca-Mo-CO₃-H₂O system at 25 °C and $[\text{C}]_T=0.01 \text{ mol/L}$. Compared with Fig.1, Fig.2 shows that the stability region of calcium molybdenum is narrower than that in Fig.1 under the given condition. The CaMoO_4 stability region is substantially replaced by CaCO_3 region when sodium carbonate is used as a leaching agent. In this region ($7.3 < \text{pH} < 8.2$), the MoO_4^{2-} concentration is almost constant.

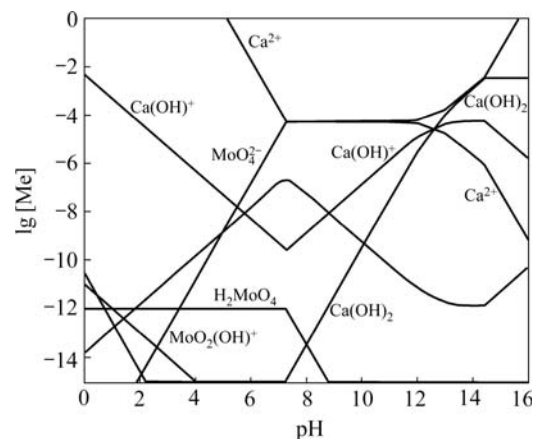


Fig.1 $\lg[\text{Me}]$ —pH diagram for Ca-Mo-H₂O system at 25 °C

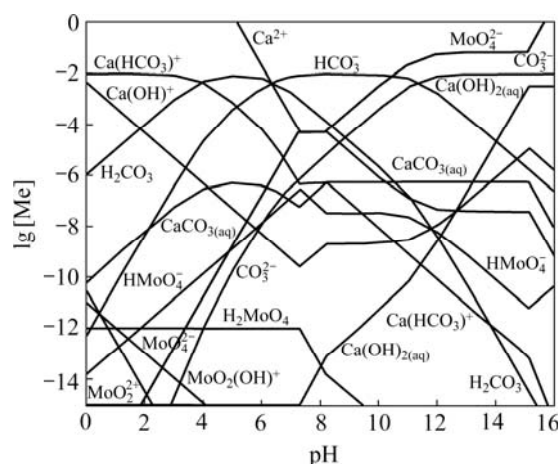
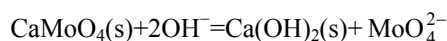


Fig.2 $\lg[\text{Me}]$ —pH diagram for Ca-Mo-CO₃-H₂O system at 25 °C and $[\text{C}]_T=0.01 \text{ mol/L}$

If pH value is lower than 7.3, most of the free carbon exists in the form HCO_3^- that reacts with Ca^{2+} to form $\text{Ca}(\text{HCO}_3)^+$. MoO_4^{2-} also turns into H_2MoO_4 precipitation. The concentrations of CO_3^{2-} and MoO_4^{2-} decrease, while the Ca^{2+} concentration increases. In fact, there is still the decomposition of calcium molybdenum by acidic medium, the same as the analysis mentioned above.

When pH value is more than 8.2, HCO_3^- transmits into CO_3^{2-} gradually. CO_3^{2-} and MoO_4^{2-} concentrations increase greatly and Ca^{2+} concentration decreases at this stage due to the solubility product constant. However, when pH value is greater than 10.3, the concentrations of MoO_4^{2-} , Ca^{2+} and CO_3^{2-} have little change. According to thermodynamic analysis, it is unnecessary to over increase pH value for decomposing molybdenum in sodium carbonate solution.

When pH value is higher than 15.1, the MoO_4^{2-} concentration increases sharply under condition of high alkalinity, and a new reaction takes place at this stage



Actually, the process of sodium carbonate decomposition turns into the sodium hydroxide decomposition at high alkalinity.

In order to investigate the effects of the variation of total dissolved carbon-containing ions concentrations on species in leaching solution, Fig.3 shows a $\lg[\text{Me}]$ —pH diagram for Ca-Mo-CO₃-H₂O system at 25°C under the condition of $[C]_{\text{T}}=1 \text{ mol/L}$.

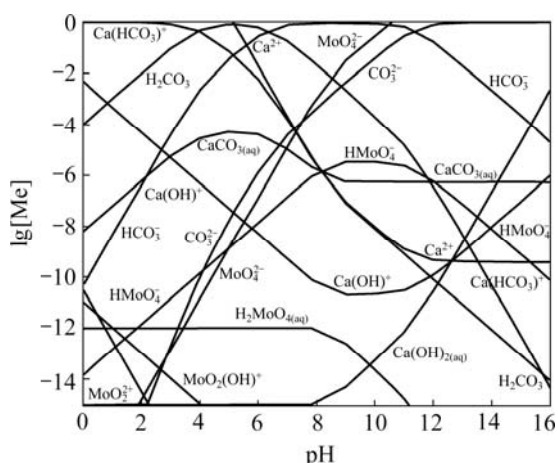


Fig.3 $\lg[\text{Me}]$ —pH diagram for Ca-Mo-CO₃-H₂O system at 25°C and $[C]_{\text{T}}=1 \text{ mol/L}$

From the above thermodynamic analysis and practical work, sodium carbonate is an effective leaching agent, which can promote the decomposing CaMoO₄ in Ca-Mo-CO₃-H₂O system.

Compared with Fig.2, Fig.3 shows that the stability region of CaMoO₄ is constricted significantly with the increase of $[C]_{\text{T}}$ and the MoO₄²⁻ concentration also increases efficiently in leaching solution. For the sake of getting best leaching yield of molybdenum in Ca-Mo-CO₃-H₂O system, certain concentration of sodium carbonate is necessary. For leaching CaMoO₄ with sodium carbonate, the higher the CO₃²⁻ concentration is, the greater the solubility of molybdenum is in theory, which has been conformed by GU et al[3] and PAN et al[6].

4 Conclusions

1) Based on principle of mass balances and thermodynamic data, $\lg[\text{Me}]$ —pH diagrams for Ca-Mo-CO₃-H₂O system at 25°C are presented, which are generated with computer under the conditions of 0.01 mol/L and 1 mol/L of total dissolved carbon-containing ions concentrations, and the diagram for Ca-Mo-H₂O system at 25°C is depicted as well.

2) Compared with the diagram of E —pH, more quantitative information on practical hydrometallurgical processes can be obtained from the given diagrams of $\lg[\text{Me}]$ —pH for Ca-Mo-CO₃-H₂O system. The stability

region of CaMoO₄ reduces significantly in the presence of Na₂CO₃. For the sake of getting best leaching yield of molybdenum, certain concentration of sodium carbonate is necessary, and dissolved sodium carbonate is an efficient leaching agent. The high total dissolved carbon-containing ions concentrations and high pH values are facilitating to decomposition of CaMoO₄.

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