A Method for Discovering the Existence of Phosphorus in Leach Liquor of Phosphorite

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Abstract In this paper, we considered a method for discovering quantitatively the existence and content of phosphorus in leach liquor of phosphorite, the mineral fertilizer resource.

Research result shows that the rate of free phosphate ions among the phosphorus in leach liquor of phosphorite is 72 to 81%, that is most of them and $H_2PO_4^-$, HPO_4^{2-} that the plant can easily absorb become fundamental thing. 19 to 28% of the phosphorus in leach liquor of phosphorite exists in the form of ion pairs, especially phosphate ion pairs combined with Ca （$CaH_2PO_4^+$, $CaHPO_4^0$） are most of them.

In case the plant absorbs the free phosphate ions and the balance of system is destroyed, these ion pairs are dissociated to free ions and let the dynamic balance of system maintain.

Key words leach liquor, phosphorite, existence, ion pair, free ion

Introduction

The great leader Comrade **Kim Il Sung** said.

"**Research in the basic sciences should be intensified. Now that science and technology are advancing at a rapid pace and the role of modern technical devices is increasing rapidly in production and construction, there is an urgent need for the basic sciences to be developed still further.**"("**KIM IL SUNG** WORKS" Vol. 35 P. 312)

One of the theoretical and practical problems in using the phosphorite as mineral fertilizer resource is to discover correctly phosphorous content that the plant can easily absorb among the various kinds of phosphorus in leach liquor of phosphorite.

It is impossible to analyze quantitatively the existent form of phosphorous compounds including free ions and ion pairs in leach liquor of phosphorite by present chemical analytical method [3, 4].

This problem can be only solved by calculation of existence of phosphorus on the basis of diagnosis model for the multi-component system [1, 2, 5].
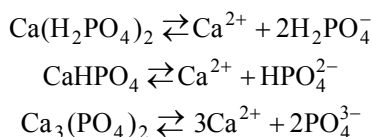
In this paper, we proposed the model that can discover quantitatively the existence and content of phosphorus and determined various kinds of phosphorous content in leach liquor of phosphorite based on this model.

1. The Theoretical Consideration for Free Ions and Ion Pairs existing in Leach Liquor of Phosphorite

Phosphorite includes various phosphates such as calcium phosphate, iron phosphate, aluminum

phosphate, etc.

Calcium phosphate that is most of these phosphates has 3 forms, i.e. calcium dihydro-genphosphate $Ca(H_2PO_4)_2$, calcium monohydrogenphosphate $CaHPO_4$, and tricalcium phosphate $Ca_3(PO_4)_2$.

$$Ca(H_2PO_4)_2 \rightleftarrows Ca^{2+} + 2H_2PO_4^-$$
$$CaHPO_4 \rightleftarrows Ca^{2+} + HPO_4^{2-}$$
$$Ca_3(PO_4)_2 \rightleftarrows 3Ca^{2+} + 2PO_4^{3-}$$

Various free phosphate ions and ion pairs in leach liquor of phosphorite exist in dynamic balance each other.

The plant absorbs only free phosphate ions such as $H_2PO_4^-$, HPO_4^{2-} among them. When the plant absorbs $H_2PO_4^-$ and HPO_4^{2-}, dynamic balance of free phosphate ions and ion pairs in solution are destroyed and ion pairs are dissociated to free ions, that maintains the dynamic balance of multi-component system.

The determination data of phosphorus in leach liquor of phosphorite shows only total phosphorus contents of free phosphate ion and ion pairs-combination of these free phosphate ions and various positive ions.

In order to calculate the content of free phosphate ions that the plant can absorb practically among phosphorus in leach liquor of phosphorite, we made diagnosis model that can discover the quantitative relationship for existence and content of free phosphate ions and ion pairs.

Ions and ion pairs necessary for making diagnosis model are shown in table 1.

Table 1.. Selected ions and ion pairs

No.	Components	Kinds	No.	Components	Kinds	No.	Components	Kinds
1	$H_2PO_4^-$	Free ion	13	OH^-	Free ion	25	$CaOH^+$	Ion pairs
2	HPO_4^{2-}	〃	14	$CaH_2PO_4^+$	Ion pairs	26	$FeSO_4^+$	〃
3	PO_4^{3-}	〃	15	$CaHPO_4^0$	〃	27	$FeOH^{2+}$	〃
4	Ca^{2+}	〃	16	$FeH_2PO_4^{2+}$	〃	28	$AlSO_4^+$	〃
5	Fe^{3+}	〃	17	$FeHPO_4^+$	〃	29	$AlOH^{2+}$	〃
6	Al^{3+}	〃	18	$AlH_2PO_4^{2+}$	〃	30	$MgCO_3^0$	〃
7	Mg^{2+}	〃	19	$MgHPO_4^0$	〃	31	$MgHCO_3^+$	〃
8	K^+	〃	20	$KHPO_4^-$	〃	32	$MgSO_4^0$	〃
9	CO_3^{2-}	〃	21	KPO_4^{2-}	〃	33	$MgOH^+$	〃
10	HCO_3^-	〃	22	$CaCO_3^0$	〃	34	KSO_4^-	〃
11	SO_4^{2-}	〃	23	$CaHCO_3^+$	〃			
12	H^+	〃	24	$CaSO_4^0$	〃			

2 Diagnosis Model for Existence of Phosphorus in Leach Liquor of Phosphorite

In order to make diagnosis model for the existence of phosphorus in leach liquor of phosphorite, some following assumptions were made.

ⅰ. Multi-component system is in static state in standard condition (T=298.15K, P=101 325Pa).

ⅱ. There exists equilibrium relationship of multi-component system at considering moment.

ⅲ. The effect of earth magnetic field is ignored.

The material balance equation for existence of phosphorus in leach liquor of phosphorite under these assumptions is as follows.

$$\left.\begin{aligned}
\sum m_{\mathrm{PO_4}} &= m_1 + m_2 + m_3 + m'_{14} + m'_{15} + m'_{16} + m'_{17} + m'_{18} + m'_{19} + m'_{20} + m'_{21} \\
\sum m_{\mathrm{Ca}} &= m_4 + m'_{14} + m'_{15} + m'_{22} + m'_{23} + m'_{24} + m'_{25} \\
\sum m_{\mathrm{Fe}} &= m_5 + m'_{16} + m'_{17} + m'_{26} + m'_{27} \\
\sum m_{\mathrm{Al}} &= m_6 + m'_{18} + m'_{28} + m'_{29} \\
\sum m_{\mathrm{Mg}} &= m_7 + m'_{19} + m'_{30} + m'_{31} + m'_{32} + m'_{33} \\
\sum m_{\mathrm{K}} &= m_8 + m'_{20} + m'_{21} + m'_{34} \\
\sum m_{\mathrm{CO_3}} &= m_9 + m'_{22} + m'_{30} \\
\sum m_{\mathrm{HCO_3}} &= m_{10} + m'_{23} + m'_{31} \\
\sum m_{\mathrm{SO_4}} &= m_{11} + m'_{24} + m'_{26} + m'_{28} + m'_{32} + m'_{34} \\
\sum m_{\mathrm{OH}} &= m_{13} + m'_{25} + m'_{27} + m'_{29} + m'_{33} \\
\sum m_{\mathrm{H}} &= m_{12}
\end{aligned}\right\} \qquad (1)$$

where, $\sum m_{\mathrm{I}}$ is the total amount of concentrations of free ions and ion pairs (mol/L), m_i is concentration of free ion (mol/L) and m'_i is concentration of ion pairs.

The relationship between the activity and concentration of each components in liquor phase is as follows.

$$a_i = \gamma_i m_i \qquad (2)$$

where, a_i is activity of i component (mol/L), m_i is concentration of i component (mol/L) and γ_i is activity coefficient of i component (mol/L), that is calculated by following formula.

$$\lg \gamma_i = -ADZ_i^2\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right) \qquad (3)$$

where, AD is Debye constant ($\lg AD = -1.150\ 83 + 93.642/T + 1.829\ 8 \cdot 10^{-3}$), Z_i is charge number of i component, I is ionic strength of solution and T is absolute temperature of solution (K).

Ionic dissociation equilibrium equation is as follows.

$$a_{14} = K_{\mathrm{CaH_2PO_4^+}} \cdot a_4 \cdot a_1, \quad a_{15} = K_{\mathrm{CaHPO_4^0}} \cdot a_4 \cdot a_2 \quad a_{16} = K_{\mathrm{FeH_2PO_4^{2+}}} \cdot a_5 \cdot a_1,$$

$$a_{17} = K_{\mathrm{FeHPO_4^+}} \cdot a_5 \cdot a_2, \quad a_{18} = K_{\mathrm{AlH_2PO_4^{2+}}} \cdot a_6 \cdot a_1, \quad a_{19} = K_{\mathrm{MgHPO_4^0}} \cdot a_7 \cdot a_2,$$

$$a_{20} = K_{\mathrm{KHPO_4^-}} \cdot a_8 \cdot a_2, \quad a_{21} = K_{\mathrm{KPO_4^{2-}}} \cdot a_8 \cdot a_3, \quad a_{22} = K_{\mathrm{CaCO_3^0}} \cdot a_4 \cdot a_9,$$

$$a_{23} = K_{CaHCO_3^+} \cdot a_4 \cdot a_{10}, \quad a_{24} = K_{CaSO_4^0} \cdot a_4 \cdot a_{11}, \quad a_{25} = K_{CaOH^+} \cdot a_4 \cdot a_{13},$$

$$a_{26} = K_{FeSO_4^+} \cdot a_5 \cdot a_{11}, \quad a_{27} = K_{FeOH^{2+}} \cdot a_5 \cdot a_{13}, \quad a_{28} = K_{AlSO_4^+} \cdot a_6 \cdot a_{11},$$

$$a_{29} = K_{AlOH^{2+}} \cdot a_6 \cdot a_{13}, \quad a_{30} = K_{MgCO_3^0} \cdot a_7 \cdot a_9, \quad a_{31} = K_{MgHCO_3^+} \cdot a_7 \cdot a_{10},$$

$$a_{32} = K_{MgSO_4^0} \cdot a_7 \cdot a_{11}, \quad a_{33} = K_{MgOH^+} \cdot a_7 \cdot a_{13}, \quad a_{34} = K_{KSO_4^-} \cdot a_8 \cdot a_{11},$$

$$a_1 = K_{H_2PO_4^-} \cdot a_{12} \cdot a_2, \quad a_2 = K_{HPO_4^{2-}} \cdot a_{12} \cdot a_3, \quad a_{10} = K_{HCO_3^-} \cdot a_{12} \cdot a_9.$$

where, K_i is thermodynamical dissociation equilibrium constant of i component. After equations (2) and (4) are substituted into equation (1), a_1, a_2, a_3, a_4, a_5, a_6, a_7, a_8, a_9, a_{10}, a_{11}, a_{12}, a_{13} are expanded and following non-linear algebraic simultaneous equations are obtained.

$$a_1 = K_{H_2PO_4^-} \cdot a_{12} \cdot a_2, \quad a_2 = K_{HPO_4^{2-}} \cdot a_{12} \cdot a_3, \quad a_3 = \gamma_{PO_4^{3-}} \cdot \left(\sum m_{PO_4} - f_{PO_4} - \frac{a_1}{\gamma_{H_2PO_4^-}} - \frac{a_2}{\gamma_{HPO_4^{2-}}} \right),$$

$$a_4 = \frac{\sum m_{Ca}}{f_{Ca}}, \quad a_5 = \frac{\sum m_{Fe}}{f_{Fe}}, \quad a_6 = \frac{\sum m_{Al}}{f_{Al}}, \quad a_7 = \frac{\sum m_{Mg}}{f_{Mg}}, \quad a_8 = \frac{\sum m_K}{f_K}, \quad a_9 = \frac{\sum m_{CO_3}}{f_{CO_3}},$$

$$a_{10} = \frac{\sum m_{HCO_3}}{f_{HCO_3}}, \quad a_{11} = \frac{\sum m_{SO_4}}{f_{SO_4}}, \quad a_{12} = \frac{a_{10}}{K_{HCO_3^-} \cdot a_9}, \quad a_{13} = \frac{\sum m_{OH}}{f_{OH}}$$

where

$$f_{PO_4} = \frac{K_{CaH_2PO_4^+} \cdot a_4}{\gamma_{14}} + \frac{K_{CaHPO_4^0} \cdot a_4}{\gamma_{15}} + \frac{K_{FeH_2PO_4^{2+}} \cdot a_5}{\gamma_{16}} + \frac{K_{FeHPO_4^+} \cdot a_5}{\gamma_{17}} +$$
$$+ \frac{K_{AlH_2PO_4^{2+}} \cdot a_6}{\gamma_{17}} + \frac{K_{MgHPO_4^0} \cdot a_7}{\gamma_{19}} + \frac{K_{KHPO_4^-} \cdot a_8}{\gamma_{20}} + \frac{K_{KPO_4^{2-}} \cdot a_8}{\gamma_{21}}$$

$$f_{Ca} = \frac{1}{\gamma_4} + \frac{K_{CaH_2PO_4^+} \cdot a_1}{\gamma_{14}} + \frac{K_{CaHPO_4^0} \cdot a_2}{\gamma_{15}} + \frac{K_{CaCO_3^0} \cdot a_9}{\gamma_{22}} + \frac{K_{CaHCO_3^+} \cdot a_{10}}{\gamma_{23}} + \frac{K_{CaSO_4^0} \cdot a_{11}}{\gamma_{24}} + \frac{K_{CaOH^+} \cdot a_{13}}{\gamma_{25}}$$

$$f_{Fe} = \frac{1}{\gamma_5} + \frac{K_{FeH_2PO_4^{2+}} \cdot a_1}{\gamma_{16}} + \frac{K_{FeHPO_4^+} \cdot a_2}{\gamma_{17}} + \frac{K_{FeSO_4^+} \cdot a_{11}}{\gamma_{26}} + \frac{K_{FeOH^{2+}} \cdot a_{13}}{\gamma_{27}}$$

$$f_{Al} = \frac{1}{\gamma_6} + \frac{K_{AlH_2PO_4^{2+}} \cdot a_1}{\gamma_{18}} + \frac{K_{AlSO_4^+} \cdot a_{11}}{\gamma_{28}} + \frac{K_{AlOH^{2+}} \cdot a_{13}}{\gamma_{29}}$$

$$f_{Mg} = \frac{1}{\gamma_7} + \frac{K_{MgHPO_4^0} \cdot a_7}{\gamma_{19}} + \frac{K_{MgCO_3^0} \cdot a_9}{\gamma_{30}} + \frac{K_{MgHCO_3^+} \cdot a_{10}}{\gamma_{31}} + \frac{K_{MgSO_4^0} \cdot a_{11}}{\gamma_{32}} + \frac{K_{MgOH^+} \cdot a_{13}}{\gamma_{33}}$$

$$f_K = \frac{1}{\gamma_8} + \frac{K_{KHPO_4^-} \cdot a_2}{\gamma_{20}} + \frac{K_{KPO_4^{2-}} \cdot a_3}{\gamma_{21}} + \frac{K_{KSO_4^-} \cdot a_{11}}{\gamma_{34}}$$

$$f_{CO_3} = \frac{1}{\gamma_9} + \frac{K_{CaCO_3^0} \cdot a_4}{\gamma_{22}} + \frac{K_{MgCO_3^0} \cdot a_7}{\gamma_{30}}$$

$$f_{HCO_3} = \frac{1}{\gamma_{10}} + \frac{K_{CaHCO_3^+} \cdot a_4}{\gamma_{23}} + \frac{K_{MgHCO_3^+} \cdot a_7}{\gamma_{31}}$$

$$f_{SO_4} = \frac{1}{\gamma_{11}} + \frac{K_{CaSO_4^0} \cdot a_4}{\gamma_{24}} + \frac{K_{FeSO_4^+} \cdot a_5}{\gamma_{26}} + \frac{K_{AlSO_4^+} \cdot a_6}{\gamma_{28}} + \frac{K_{MgSO_4^0} \cdot a_7}{\gamma_{32}} + \frac{K_{KSO_4^-} \cdot a_8}{\gamma_{34}}$$

$$f_{OH} = \frac{1}{\gamma_{13}} + \frac{K_{CaOH^+} \cdot a_4}{\gamma_{25}} + \frac{K_{FeOH^{2+}} \cdot a_5}{\gamma_{27}} + \frac{K_{AlOH^{2+}} \cdot a_6}{\gamma_{29}} + \frac{K_{MgOH^+} \cdot a_7}{\gamma_{33}}$$

The calculation is performed by simple iterative method and convergence condition of calculation process is as follows.

$$\lim_{k \to \infty} \left| a_i^{k+1} - a_i^k \right| \le \varepsilon$$

where ε is tolerance limit.

3. Calculation Result and Analysis

Calculation result for contents of free phosphate ions and ion pairs in leach liquors of some phosphorite by 0.2mol/L hydrochloric acid is presented in table 2 and 3.

Table 2. Concentration of free phosphate ions (mol/L)

Division	$H_2PO_4^-$	HPO_4^{2-}	PO_4^{3-}
1	4.41×10^{-2}	7.68×10^{-3}	5.16×10^{-9}
2	7.16×10^{-2}	12.89×10^{-3}	8.43×10^{-9}
3	11.38×10^{-2}	20.17×10^{-3}	1.33×10^{-9}

As shown in table 2 and 3, though the rate of free phosphate ions among the phosphorus in leach liquor of phosphorite is different according to samples, 72 to 81% is most of phosphorus of leach liquor. $H_2PO_4^-$, HPO_4^{2-} that the plant can easily absorb are most of them.

Among them, the content of ion $H_2PO_4^-$ is 5.6 times greater than content of ion HPO_4^{2-}.

Table 3. Concentration of phosphate ion pairs (mol/L)

Division	$CaH_2PO_4^+$	$CaHPO_4^0$	$FeH_2PO_4^{2+}$	$FeHPO_4^+$	$AlH_2PO_4^{2+}$	$MgHPO_4^0$	$KHPO_4^-$
1	1.14×10^{-2}	5.70×10^{-3}	3.18×10^{-10}	0.71×10^{-8}	35.83×10^{-11}	1.07×10^{-5}	1.39×10^{-9}
2	0.15×10^{-2}	31.11×10^{-3}	51.76×10^{-10}	35.17×10^{-8}	3.79×10^{-11}	21.36×10^{-5}	2.45×10^{-9}
3	1.93×10^{-2}	12.10×10^{-3}	0.73×10^{-10}	4.52×10^{-8}	4.37×10^{-11}	2.78×10^{-5}	44.17×10^{-9}

Among the phosphorus in leach liquor of phosphorite, 19 to 28% exist in form of ion pairs, especially, phosphate ion pairs combined with Ca ($CaH_2PO_4^+$, $CaHPO_4^0$) are most of them. In case the plant absorbs the free phosphate ions and the balance of system is destroyed, these ion pairs are dissociated to free ions and let the dynamic balance of system maintain.

Conclusion

In this paper, we considered quantitatively the existence and content of phosphorus in leach liquor of phosphorite.

The rate of free phosphate ions among the phosphorus in leach liquor of phosphorite is 72 to 81% and the rate of form of ion pairs is 19 to 28%.

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