

APPLIED CHEMISTRY

Solution Chemistry Study of Salt-type Mineral Flotation Systems: Role of Inorganic DispersantsHu Yuehua,[†] Ruan Chi,[‡] and Zhenghe Xu^{*‡}

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Interactions of salt-type minerals with common inorganic flotation depressants were investigated through solution chemistry calculations. From the constructed conditional solubility product limits and the actual solubility product lines of calcium silicate and phosphate in fluorite, calcite, and apatite single-mineral systems, the critical precipitation pH or concentration of silicate and phosphate in the corresponding mineral suspensions was determined. These values provided a fundamental basis for interpreting the results of flotation tests and were in line with the results of ζ -potential and dispersant adsorption measurements. The surface precipitation of calcium silicate or phosphate on fluorite and calcite was identified as a major depression mechanism. Selective depressing conditions for different salt-type minerals using Na_2SiO_3 and Na_3PO_4 as depressants were determined on the basis of solution chemistry calculations of the systems.

Introduction

Salt-type minerals are characterized by their relatively high solubilities, which are lower than the solubilities of simple salt minerals such as halite and sylvite but higher than the solubilities of most oxides and silicate minerals. Typical minerals in this category include fluorite (CaF_2), barite (BaSO_4), calcite (CaCO_3), apatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$], and scheelite (CaWO_4). In natural mineral deposits, many of these salt-type minerals are associated with each other, and their separation by flotation is difficult because of their similar responses to flotation reagents. This similarity is often attributed to their comparable surface chemical compositions and, in many cases, to the high surface activities of collectors employed to float them.^{1–5} The use of inorganic modifying agents such as sodium silicate and phosphate is therefore essential to achieve a desired level of selectivity in these systems.^{6–11} Numerous investigations have been conducted to study collecting mechanisms in view of crystal structures, electrokinetics, and collector adsorption or reaction.^{12–20} In comparison, fewer studies have focused on investigating the interactions of flotation modifiers with minerals.

Solution chemistry calculations have been shown to be a powerful tool for studying interaction mechanisms of collectors with salt-type minerals. The pioneering work demonstrated that solution chemistry considerations can lead to predictions of the theoretical point of zero charge (PZC) of oxides and calcite.^{21,22} Chemical speciation diagrams of metal hydroxy ions were used

to explain the activation mechanism of metal ions in silicate flotation with anionic collectors.²³ The critical pH for flotation separation of calcium- and iron-containing ores was determined from the solubility limits of the corresponding iron and calcium compounds.² During the past two decades, solution chemistry calculations have been used to study dissolution/precipitation characteristics, surface species conversion,^{24,25} electrokinetics of minerals,²⁶ active species of collector and/or chelating flotation agents,^{27,28} and interaction mechanisms of collectors with minerals. The fundamental study of solution chemistry calculations has led to predictions of the optimal flotation pH range, optimal collector concentration, and even optimal flotation separation conditions.^{28–34} Our previous studies showed that the conditional solubility product of a metal–flotation reagent system serves as a useful guideline for determining the chemical interactions between minerals and reagents.^{32–34} For example, the optimal pH for wolframite flotation using sodium oleate or hydroximate as the collector was experimentally determined to be at the pH that corresponds to the minimum conditional solubility product of Mn/Fe-collector salts.³²

This paper provides a systematic solution chemistry investigation of salt-type minerals in target modifier solutions in an attempt to understand the role of modifiers in modifying collector–mineral interactions. The knowledge derived from this study could eventually lead to the determination of optimum conditions for selective depression and improved flotation separation.

Experimental Section

Materials. Mineral samples of apatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$], fluorite (CaF_2) and calcite (CaCO_3) were hand-picked carefully from Wangji Mine, Dongfeng Mine, and Changsha powder factory (all in China), respectively.

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Table 1. Calcium Hydrolysis and Silicate Protonation Reactions and Corresponding Equilibrium Constants³⁶

species	Ca ²⁺		SiO ₃ ²⁻	
reactions	Ca ²⁺ + OH ⁻ = CaOH ⁺	$K_1 = 10^{1.4}$	H ⁺ + SiO ₃ ²⁻ = HSiO ₃ ⁻	$K_1^H = 10^{12.56}$
	Ca ²⁺ + 2OH ⁻ = Ca(OH) ₂	$K_2 = 10^{2.77}$	H ⁺ + HSiO ₃ ⁻ = H ₂ SiO ₃	$K_2^H = 10^{9.43}$
coefficient	$\alpha_{Ca} = 1 + K_1[OH^-] + K_2[OH^-]^2$		$\alpha_{Si} = 1 + K_1^H[H^+] + K_1^H K_2^H [H^+]^2$	

The single-mineral samples were ground in a laboratory porcelain mill. The ground samples were sieved, and the -74- μ m size fraction was collected and used in flotation tests and modifier adsorption studies. A portion of the -74- μ m size fraction particles was further ground in an agate mortar to -5 μ m and used in electrophoretic mobility measurements. Quantitative chemical analysis of the samples showed that the purity of all samples was greater than 95%. The surface area for the -74- μ m size fraction particles was determined by the nitrogen adsorption method (BET) to be 2.13, 0.56, and 0.89 m²·g⁻¹ for apatite, fluorite, and calcite, respectively.

Sodium phosphate (Na₃PO₄) and silicate (Na₂SiO₃·9H₂O) were used as modifiers, and sodium oleate was used as the collector. The sodium silicate used in this study had a SiO₂-to-Na₂O molar ratio of 1 to 1. The pH of the testing solutions was adjusted with NaOH or HCl. All chemicals were of analytical grade and were used without further purification. Doubly distilled water was used in all experiments unless stated otherwise.

Electrokinetic Measurements. The electrophoretic mobility of mineral suspensions was measured at 298 ± 2K using an MRK electrophoresis apparatus equipped with a flat cell. Mineral suspensions containing 0.05% solids were conditioned in a beaker for 15 min at a given pH and modifier concentration in a 1 mM KNO₃ background electrolyte solution. By means of a medical syringe, the electrophoresis cell was filled with the conditioned suspensions. About 40 different particles were counted to obtain an average electrophoretic mobility from which the ζ -potential was calculated using the Smoluchowski equation.

Modifier Adsorption Measurements. Suspensions containing 1 g of the -74- μ m size fraction of the minerals in 50 mL of sodium silicate solution at a given pH were stirred for 30 min at room temperature in a 150-mL beaker. A sample of each suspension was taken and centrifuged at 3000 rpm for 15 min. The residual concentration of sodium silicate in the separated supernatant was determined using the calorimetric method of Shin.³⁵ The difference between the initial and equilibrium sodium silicate concentrations was considered as the amount of the sodium silicate adsorbed onto the mineral sample and was normalized by the surface area of the added particles.

Flotation Tests. Single-mineral flotation tests were carried out in a micro-flotation cell. Mineral suspensions were prepared by adding 2.0 g of the -74- μ m size fraction of the minerals to 50 mL of solution under agitation with a magnetic stirrer. The pH of the mineral suspensions was first adjusted to a desired value by adding concentrated NaOH or HCl stock solution. The prepared modifier stock solution was added to the desired concentration during conditioning for 3 min. Sodium oleate solution was then added, and the resulting suspension was conditioned for an additional 2 min without aeration, followed by flotation for a total of 4 min. The floated and unfloated particles were collected, filtered, and dried in an air-ventilated oven at 120 °C. The recovery was calculated on the basis of solid weight distributions between the two products.

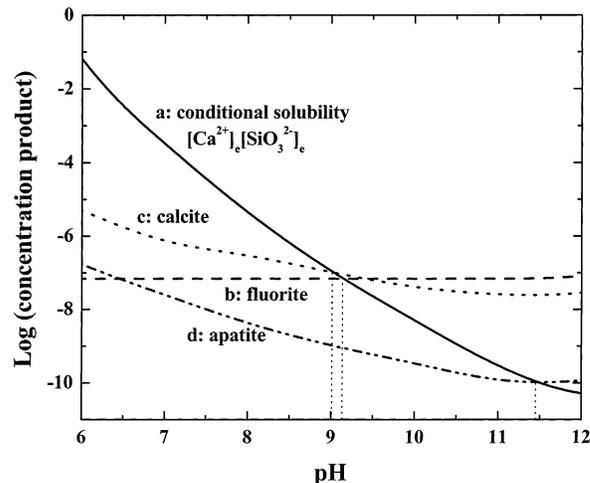
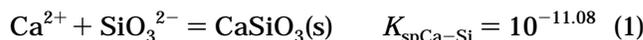


Figure 1. Conditional solubility product limit of (a) calcium silicate and actual calcium silicate product lines of (b) fluorite, (c) calcite, and (d) apatite suspensions containing 0.3 mM sodium silicate. The vertical lines indicate the critical pH's of bulk calcium silicate precipitation in corresponding mineral suspensions.

Results and Discussion

Solubility Diagram for the Calcium Silicate System. At an ionic concentration above the solubility product limit, the formation of calcium silicate in a solution containing Ca²⁺ and SiO₃²⁻ can be expressed by the equation



where $K_{\text{spCa-Si}}$ is the corresponding solubility product constant, with the value being taken from refs 36 and 37. Reaction 1 defines the solubility product limit. According to coordination chemistry, the conditional solubility product of reaction 1 is given by

$$L_{\text{spCa-Si}} = [\text{Ca}^{2+}]_e [\text{SiO}_3^{2-}]_e = K_{\text{spCa-Si}} \alpha_{\text{Ca}} \alpha_{\text{Si}} \quad (2)$$

where $[\text{Ca}^{2+}]_e$ and $[\text{SiO}_3^{2-}]_e$ are, respectively, the total soluble calcium and silicate concentrations in solution. The α 's in eq 2 is the overall coefficient of a given species, with subscripts Ca and Si representing calcium and silicate, respectively. The pertinent calcium hydrolysis and silicate protonation reactions are summarized in Table 1.

Considering all of the hydrolysis and protonation reactions and using the thermodynamic data in Table 1, the conditional solubility product limit of calcium silicate as a function of pH was calculated, and the results are shown in Figure 1 by curve a. In this figure, the region above the curve indicates the conditions under which bulk calcium silicate precipitation would occur. According to the principles of solution chemistry, bulk precipitation of calcium silicate is anticipated when $[\text{Ca}^{2+}]_T [\text{SiO}_3^{2-}]_T \geq L_{\text{spCa-Si}} = [\text{Ca}^{2+}]_e [\text{SiO}_3^{2-}]_e$, where $[\text{Ca}^{2+}]_T$ and $[\text{SiO}_3^{2-}]_T$ are, respectively, the total calcium and silicate concentration in solution.

Critical Conditions of Calcium-Containing Mineral-Silicate Systems. To understand the selec-

Table 2. Pertinent Reactions and Thermodynamic Data for Calculating the Total Calcium Concentration for Salt-type Mineral Systems^a

mineral	pertinent reactions and constant	
fluorite (CaF ₂)	$[Ca^{2+}]_T = (K_{spCa-F} \alpha_{Ca} \alpha_F^{2/4})^{1/3}$ $H^+ + F^- = HF$ $\alpha_F = 1 + K^H[H^+]$	$K_{spCa-F} = [Ca^{2+}][F^-]^2 = 10^{-10.41}$ $K^H = 10^{3.4}$
calcite (CaCO ₃)	$[Ca^{2+}]_T = (K_{spCa-C} \alpha_{Ca} \alpha_C)^{1/2}$ $H^+ + CO_3^{2-} = HCO_3^-$ $2H^+ + CO_3^{2-} = H_2CO_3$ $\alpha_C = 1 + K_1^H[H^+] + K_2^H[H^+]^2$	$K_{spCa-C} = [Ca^{2+}][CO_3^{2-}] = 10^{-8.35}$ $K_1^H = 10^{10.33}$ $K_2^H = 10^{16.68}$
apatite [Ca ₁₀ (PO ₄) ₆ (OH) ₂]	$\log[Ca^{2+}]_T = \frac{1}{16}(\log K_{spCa-Ap} \alpha_{Ca}^{10} \alpha_p^6) - \frac{1}{8}pH + 1.83$ $H^+ + PO_4^{3-} = HPO_4^{2-}$ $2H^+ + PO_4^{3-} = H_2PO_4^-$ $3H^+ + PO_4^{3-} = H_3PO_4$ $\alpha_p = 1 + K_1^H[H^+] + K_2^H[H^+]^2 + K_3^H[H^+]^3$	$K_{spCa-Ap} = 10^{-115}{}^b$ $K_1^H = 10^{12.35}$ $K_2^H = 10^{19.55}$ $K_3^H = 10^{21.7}$

^a All constants taken from ref 36 unless otherwise indicated. ^b Reference 24.

tive depression of calcium-containing salt-type minerals by sodium silicate using the above conditional solubility limit diagram, the soluble calcium concentrations in various mineral systems must be determined. This can be accomplished by considering the solubility limits of the minerals. It is conceivable that calcium ions dissolved from salt-type minerals react with silicate in a pulp to form calcium silicate. The extent of reaction depends on the concentration of added silicate and the total concentration of calcium ions dissolved. The total concentration of calcium ions dissolved can be calculated from the conditional solubility product of the minerals. For fluorite, for example, the total calcium ion concentration is given by

$$[Ca^{2+}]_T = (K_{spCa-F} \alpha_{Ca} \alpha_F^{2/4})^{1/3} \quad (3)$$

where K_{spCa-F} is the solubility product of fluorite. The reported value of K_{spCa-F} is $10^{-10.41}$. The value of α_{Ca} can be calculated using the equation given in Table 1. Because fluoride in water undergoes hydrolysis, the coefficient α_F is governed by the hydrofluoric acid dissociation reaction shown in Table 2 and is given by

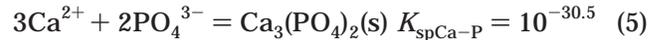
$$\alpha_F = 1 + K^H[H^+] \quad (4)$$

Using eq 3 and the thermodynamic data given in Table 2, the total soluble calcium concentration for fluorite can be calculated as a function of pH. For a fixed silicate concentration of $80 \text{ mg}\cdot\text{L}^{-1}$ or 0.3 mM , the actual calcium silicate product line can be constructed as shown by dashed curve b in Figure 1. It is important to note that, when the actual calcium silicate product line of the mineral falls below the conditional solubility product limit curve a, calcium silicate bulk precipitates are unlikely to form in the mineral suspension. The crossover point of the two curves defines a critical pH above which calcium silicate bulk precipitates are anticipated to form. In the case of fluorite, the critical pH is found to be at pH 9.2, as marked by the vertical dotted line in Figure 1. The significance of the critical pH is that, for a saturated mineral suspension at a pH greater than its critical pH, the condition of $[Ca^{2+}]_T - [SiO_3]_T > [Ca^{2+}]_e [SiO_3^{2-}]_e$ is satisfied, and the bulk precipitation of calcium silicate is anticipated. The current results suggest that the formation of calcium silicate on fluorite and hence the depression of fluorite flotation by 0.3 mM sodium silicate are feasible at pH's above 9.2.

Similar analyses can be applied to other calcium-containing minerals, and the relevant equations with pertinent constants are summarized in Table 2. From

the data given in this table, the actual calcium silicate product lines for calcite and apatite are constructed and shown in Figure 1 as curves c and d, respectively. From this figure, flotation depressions of calcite and apatite are anticipated at pH's above 9.0 and 11.5, respectively. These results suggest that the flotation separation of apatite by the selective depression of fluorite and calcite flotation at pH's greater than 9.2 but lower than 11.5 is feasible when sodium silicate is used as the depressant. It is also evident that the flotation separation of fluorite from calcite is extremely difficult if not impossible when sodium silicate is used as the depressant.

Solubility Diagram for Calcium Phosphate System. To compare the effectiveness of different depressants in salt-type mineral flotation systems, solution chemistry calculations were extended to the phosphate system. For illustration purposes, only the fluorite mineral system is considered in this study. The precipitation of calcium phosphate in a solution containing Ca^{2+} and PO_4^{3-} is described by the reaction



with the corresponding conditional solubility product being given by

$$L_{spCa-P} = [Ca^{2+}]_e^3 [PO_4^{3-}]_e^2 = K_{spCa-P} \alpha_{Ca}^3 \alpha_p^2 \quad (6)$$

where $[Ca^{2+}]_e$ and $[PO_4^{3-}]_e$ are, respectively, the total soluble calcium and phosphate concentrations and α_p is the coefficient of the phosphate protonation reactions. The value of α_p is determined from the various protonation reactions described in Table 2. Applying the thermodynamic data given in Table 2 to conditional solubility product eq 6, the conditional solubility product limit of $Ca_3(PO_4)_2$ as a function of pH was calculated, and the results are shown in Figure 2 by curve a. The bulk precipitation of calcium phosphate is anticipated when $[Ca^{2+}]_T^3 [PO_4^{3-}]_T^2 \geq K_{spCa-P} \alpha_{Ca}^3 \alpha_p^2 = [Ca^{2+}]_e^3 [PO_4^{3-}]_e^2$, i.e., in the region above the curve. Here, $[Ca^{2+}]_T$ and $[PO_4^{3-}]_T$ are the total soluble calcium and phosphate concentrations, respectively.

Applying eq 6 along with the pertinent phosphate protonation reactions described in Table 2 to a fluorite-saturated suspension containing 0.1 mM sodium phosphate, the actual calcium phosphate product line can be constructed as shown in Figure 2 by curve b. It is evident that, at $pH > 7.2$, the condition of $[Ca^{2+}]_T^3 [PO_4^{3-}]_T^2 > [Ca^{2+}]_e^3 [PO_4^{3-}]_e^2$ is satisfied, indicating the formation of bulk calcium phosphate precipitates in the fluorite suspension. Also shown in Figure 2 is the solubility product limit curve c of calcium metaphos-

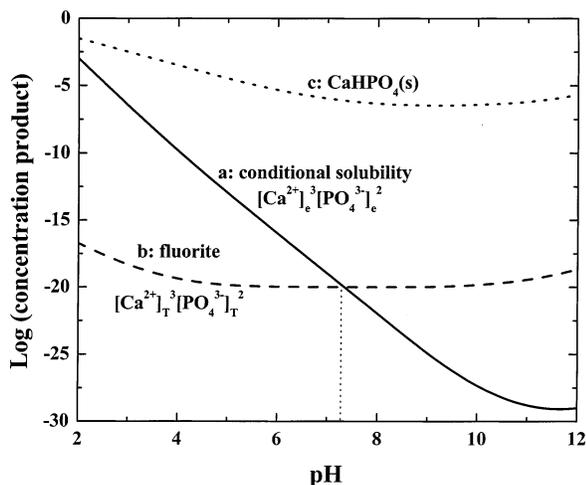


Figure 2. Conditional solubility product limits of (a) calcium phosphate and (b) calcium metaphosphate and (c) actual calcium phosphate product line of a fluorite suspension containing 0.1 mM sodium phosphate. The vertical line indicates the critical pH for calcium phosphate precipitation in the fluorite suspension.

phate $[\text{CaHPO}_4(\text{s})]$, calculated using procedures similar to those described above. This curve lies well above the other two curves, suggesting that the precipitation of calcium metaphosphate is unlikely to occur in the current system. Comparing Figures 1 and 2, it is evident that sodium phosphate is a stronger depressant, as calcium phosphate precipitation in a fluorite suspension containing 0.1 mM sodium phosphate is anticipated at pH's greater than 7.2, in contrast to the precipitation of calcium silicate at pH's greater than 9.2 in 0.3 mM sodium silicate solutions. The practical importance of this finding is that a phosphate type of depressant should be considered to depress fluorite and calcite flotation in a neutral pH suspension for selective apatite flotation.

It should be noted that solution chemistry calculations simultaneously consider all reactions occurring in a solution. They are therefore accurate in predicting the conditions of bulk precipitation. The results can also serve as a good guideline for predicting surface precipitation in a given mineral system. It has been demonstrated^{12,13} that several reactions similar to the bulk reactions could occur at the solid-liquid interface. These reactions can play a governing role in determining the ultimate surfactant adsorption and flotation. In fact, precipitation in the interfacial region is controlled by the solubility product limit of bulk solution precipitation, although it often occurs at lower solubility limits.^{18,20} Therefore, it is not unreasonable to consider bulk-precipitation conditions as a lower limit for surface precipitation.

Sodium Silicate Adsorption. To confirm the selective surface precipitation of calcium silicate on various calcium-containing salt-type minerals, the adsorptions of sodium silicate on fluorite, calcite, and apatite were measured. The amounts of the silicate adsorbed on various mineral surfaces from a 0.3 mM sodium silicate solution are shown in Figure 3. Qualitatively, the silicate adsorptions measured on various minerals followed the same trend as anticipated from the results of solution chemistry calculations, i.e., the amount of silicate adsorbed on fluorite was greater than the amount adsorbed on calcite, which was much greater than the amount adsorbed on apatite. It appears that the pH corresponding to a significant increase in silicate

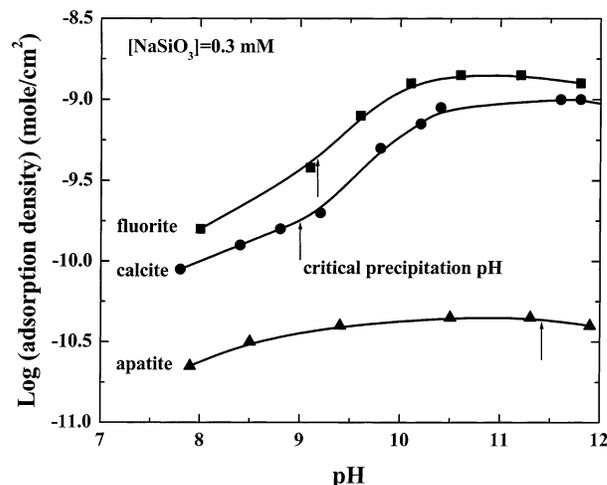


Figure 3. Adsorption of silicate onto fluorite, calcite, and apatite from a 0.3 mM sodium silicate solution. The arrows indicate the calculated critical calcium silicate pH's for precipitation from the corresponding mineral suspensions.

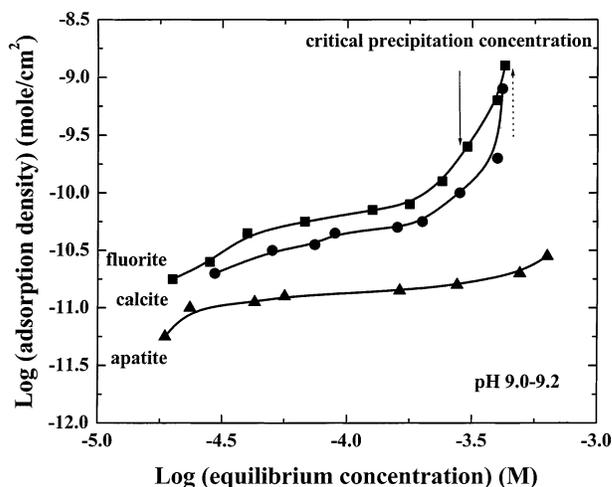


Figure 4. Adsorption isotherms of silicate on fluorite, calcite, and apatite measured at a suspension pH of 9.0. The upward arrow represents the calculated critical concentration for calcium silicate precipitation from a calcite suspension.

adsorption on a given mineral corresponded well with the critical pH predicted from the solution chemistry calculations. For fluorite (squares), for example, a significant increase in silicate adsorption started at a pH of around 9, which is just slightly lower than the predicted critical pH of 9.2 (indicated by the arrow) for bulk calcium silicate precipitation in this mineral system. The slight shift toward lower surface precipitation pH is consistent with the expectation of surface precipitation occurring prior to the corresponding bulk precipitation. A similar shift is evident for calcite. Silicate adsorption on apatite (triangles) can be considered marginal over the pH range studied. This is anticipated for this system with a much lower actual calcium silicate product line that is close to the conditional solubility product limit of calcium silicate (curve a in Figure 1).

To further illustrate the importance of solution chemistry calculations, silicate adsorption isotherms at pH 9.0–9.2 were determined. The results presented in Figure 4 confirm that silicate adsorption/precipitation on fluorite is slightly greater than that on calcite, which is much greater than that on apatite. Considering the similar calcium silicate product lines in the fluorite-

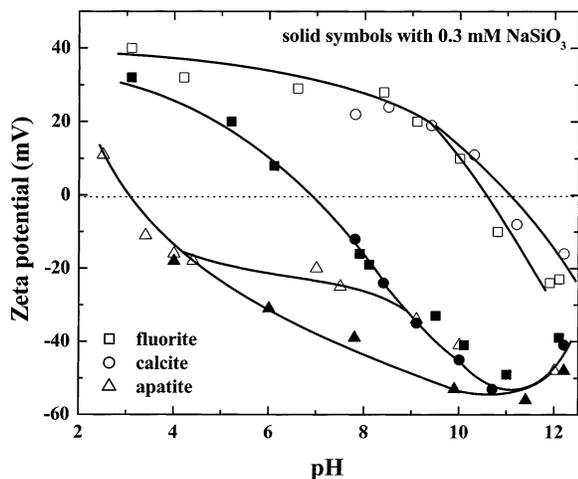


Figure 5. ζ -potentials of fluorite, calcite, and apatite measured in the absence (open symbols) and presence (solid symbols) of 0.3 mM sodium silicate.

and calcite–silicate systems, which is much higher than that in the apatite–silicate system as shown in Figure 1, this trend is not unexpected. For a given mineral system, a critical silicate concentration appears to exist for effective silicate adsorption. For the convenience of discussion, we define this concentration as the critical surface precipitation concentration (cspc). To understand the existence of the cspc and its variations with different minerals, it is instructive to calculate the critical silicate concentration for bulk calcium silicate precipitation. For a salt-type mineral system at a given pH, the critical bulk precipitation concentration (cbpc) is governed by the solubility boundary condition

$$[\text{SiO}_3^{2-}]_{\text{T}} \geq K_{\text{spCa-Si}} \alpha_{\text{Ca}} \alpha_{\text{Si}} / [\text{Ca}^{2+}]_{\text{T}} \quad (7)$$

At pH 9, the cbpc was calculated to be $10^{-3.3}$ M for fluorite, $10^{-3.45}$ M for calcite, and $10^{-1.73}$ M for apatite. For illustrative purpose, the calculated cbpc for fluorite is indicated in Figure 4 by the dotted arrow line. This concentration is much higher than the corresponding cspc of ca. $10^{-3.6}$ M indicated by the solid arrow line. This finding further confirms that the adsorption or surface precipitation of calcium silicate on fluorite occurs at a much lower silicate concentration than that needed for bulk calcium silicate precipitation. A similar observation can be made for calcite. These observations are consistent with many other reports that show similar trends.^{11,18,19} For apatite, on the other hand, the calculated cbpc is beyond the concentration range covered in this adsorption study. This finding suggests that the precipitation of calcium silicate on apatite at this pH might not occur, which is consistent with the measured extremely low sodium silicate adsorption density shown in Figure 4.

Electrokinetic Potential. To illustrate the role of silicate adsorption in salt-type mineral depression, ζ -potentials of fluorite, calcite, and apatite as functions of pH were measured, and the results are summarized in Figure 5. In the absence of sodium silicate (open symbols), an isoelectric point (iep) of pH 10.5 was obtained for fluorite (open squares). This value is within the range of iep values of pH 10–10.5, reported by Miller.³⁷ A similar iep of pH 11 was obtained for calcite (open circles). For apatite (open triangles), the iep is much lower at pH 3.2. These iep values are in excellent agreement with those reported by Pugh¹⁷ and Mishra.⁹

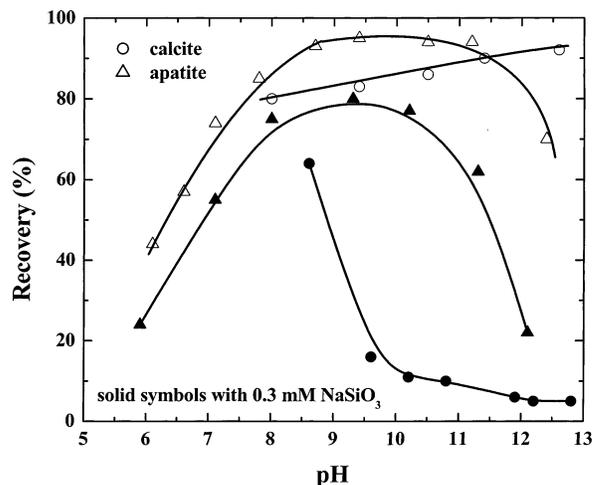


Figure 6. Flotation recovery of calcite and apatite in the absence (open symbols) and presence (solid symbols) of 0.3 mM sodium silicate using 0.1 mM sodium oleate as the collector.

In the presence of 0.3 mM sodium silicate (solid symbols), a significant shift in iep from 10.5 to 7.0 was observed for fluorite. The measured ζ -potential (solid triangles) became much more negative or much less positive over a wide pH range above 5. However, the largest gap induced by sodium silicate addition was observed at pH 9, which corresponded extremely well with the calculated critical pH of calcium silicate precipitation in fluorite suspensions (Figure 1). For calcite in 0.3 mM sodium silicate solution, the iep was not measured over the operational pH range above 7.8, below which significant dissolution of calcite made ζ -potential measurements impractical. The measured ζ -potential became much more negative, with the largest gap also being observed at the corresponding critical calcium silicate precipitation pH of 9. It is also interesting to note that, in the presence of sodium silicate, the ζ -potentials for fluorite and calcite became indistinguishable at pH's above 8. This finding suggests the adsorption/surface precipitation of calcium silicate to be the depression mechanism of fluorite and calcite flotation by sodium silicate. In contrast to fluorite and calcite, the change in ζ -potential by sodium silicate addition is much less significant for apatite, as shown by the triangles in Figure 5. This observation is consistent with the observed much lower silicate adsorption density on apatite than on fluorite and calcite shown in Figure 3.

Flotation. To demonstrate the application of solution chemistry calculations to the interpretation/prediction of mineral flotation results, single-mineral flotation tests were conducted. For illustrative purpose, the results for the single-mineral flotations of calcite and apatite using 0.1 mM sodium oleate as the collector in the absence and presence of 0.3 mM sodium silicate depressants are shown in Figure 6. Without addition of the depressant, both calcite and apatite floated well over a wide pH range, as shown by the open symbols. The addition of 0.3 mM sodium silicate depressed calcite flotation, with complete depression being observed at pH's above 9 (filled circles). This pH correlates extremely well with the critical pH for calcium silicate precipitation on calcite shown in Figure 1. For apatite, a significant depression was observed at pH's above 11.5 as shown in Figure 6 by the filled triangles. Again, this pH corresponds well with the critical pH of calcium silicate precipitation on apatite derived from solution chemistry

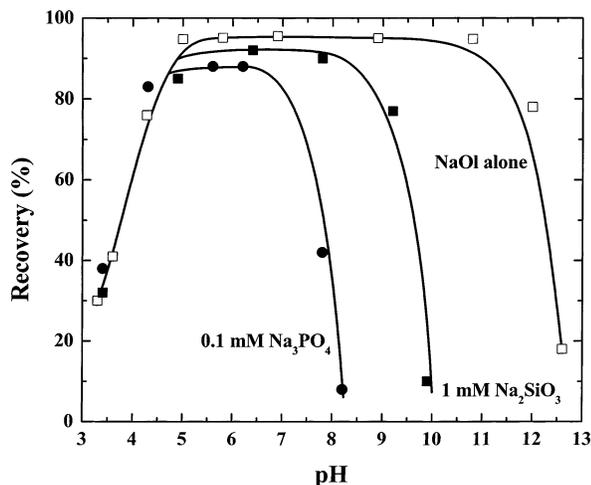


Figure 7. Flotation recovery of fluorite in the absence (open squares) and presence of 1 mM sodium silicate (solid squares) or 0.1 mM sodium phosphate (solid circles) using 0.1 mM sodium oleate as the collector.

calculations. The flotation depression characteristics observed here are consistent with observations made in silicate adsorption and ζ -potential measurements. It is evident that selective depression of calcite by sodium silicate in apatite flotation is feasible at pH's above 9 but below 11.5, as predicted from the above solution chemistry calculations.

The role of different depressants in fluorite flotation was investigated, and the results of fluorite flotation using 0.1 mM oleate as the collector in the absence and presence of sodium silicate and phosphate are shown in Figure 7. Without addition of the depressant (open squares), fluorite floated well over a wide pH range of 5–11. With the addition of 1 mM sodium silicate, fluorite flotation at pH's above 9.0 was drastically depressed. A much greater reduction in the critical flotation pH to 7.0 was observed when 0.1 mM sodium phosphate was added. It is not surprising to observe that the upper pH limits of 9.0 and 7.0 for fluorite flotation in the presence of the depressants correspond well with the predicted critical precipitation pH's of 9.2 and 7.2 for calcium silicate and phosphate on fluorites, as shown in Figures 1 and 3, respectively.

The current study clearly demonstrates that solution chemistry calculations are a useful tool for predicting depression conditions and studying depression mechanisms of inorganic depressants in salt-type mineral flotation systems. They allow for the selection of suitable flotation systems and conditions for the desired separations. For example, solution chemistry calculations (Figure 1) showed that the selective depression of fluorite and calcite for apatite flotation can be accomplished at pH's above 9.2 but below 11.5 in the presence of 0.3 mM sodium silicate. The single-mineral flotation results in Figure 6 confirmed this prediction. Solution chemistry calculations also showed that sodium phosphate is a stronger depressant than sodium silicate in fluorite flotation. The former is capable of depressing fluorite flotation at a lower concentration over a wider suspension pH range than the latter. This prediction was confirmed by the flotation results shown in Figure 7.

Conclusions

By applying solution chemistry calculations to a salt-type mineral and inorganic depressant flotation system,

the critical depression pH and depressant concentration were derived. The critical calcium silicate precipitation pH's for fluorite, calcite, and apatite in a 0.3 mM silicate solution were found to be 9.2, 9.0, and 11.5, respectively. At pH 9, the critical silicate concentrations for calcium silicate precipitation in fluorite, calcite, and apatite mineral systems were found to be $10^{-3.3}$, $10^{-3.45}$, and $10^{-1.75}$ M, respectively. The predicted selective depression of fluorite and calcite for apatite flotation at pH's above 9 but below 11.5 was confirmed by silicate adsorption studies, ζ -potential measurements, and single-mineral flotation tests. Solution chemistry calculations also revealed that phosphate in fluorite suspensions exhibits a lower critical precipitation pH of 7.2 at a lower phosphate concentration (0.1 mM), indicating stronger depressive action than silicate and resulting in a narrower flotation pH window from pH 4 to pH 6. On the basis of the adsorption and ζ -potential measurements, along with the solution chemistry calculations, surface precipitation of calcium silicate or calcium phosphate was identified to be the major depression mechanism of fluorite and calcite in apatite flotation using oleate as the collector. In this study, solution chemistry calculations have been further shown to be a useful tool for predicting optimal flotation separation conditions and explaining depression mechanisms of inorganic depressants.

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