PHYSICOCHEMICAL ANALYSIS OF INORGANIC SYSTEMS

Phase Equilibria in the V₂O₅–NaVO₃–Ca(VO₃)₂–Mn₂V₂O₇ System and Interactions of Phases with H₂SO₄ and NaOH Solutions

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Abstract—Phase composition of the V₂O₅–NaVO₃–Ca(VO₃)₂–Mn₂V₂O₇ system was studied, and a subsolidus phase diagram constructed. The tetrahedration of the diagram is determined by the fact that the end-member of Ca_{1-x}Mn_x(VO₃)₂ solid solution is in equilibrium with all compounds of the system (V₂O₅, NaVO₃, Ca(VO₃)₂), vanadium β-bronzes Na_xV₂O₅ (0.22 $\leq x \leq 0.40$) and κ -bronzes (0.25 $\leq x \leq 0.45$, $0 \leq y \leq 0.16$), Mn₂V₂O₇, and Na₂Mn₃(V₂O₇)₂ and with the end-members of reciprocal solid solutions based on calcium and sodium metavanadates. At 20°C, the degree of vanadium dissolution α for Na₂Ca(VO₃)₄ is 100% for 0.5 \leq pH \leq 10; for the other phases of the system, vanadium dissolution ranges from 100 to 10% for pH below 3.5; in the alkaline pH range, $\alpha \leq 10\%$. Sodium for calcium substitution in Ca(VO₃)₂ increases α in aqueous NaOH to 20%. For Na₂Mn₃(V₂O₇)₂, α decreases from 92 to 80% as pH changes from 0.5 to 2.5; at pH above 4, $\alpha = 30\%$.

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Vanadium ores and industrial wastes contain considerable calcium and manganese levels in addition to iron, magnesium, nickel, silicon, titanium, chromium, and aluminum. Most vanadium is involved in phases with corundum $(Fe_{1-x}V_{x})_{2}O_{3}$ or pyroxene $M_{2}Si_{2}O_{6}$ structure, in which vanadium, chromium, and aluminum substitute isomorphically for silicon; together with manganese and calcium, vanadium is involved in spinel $M^{2+}M_2^{3+}O_4$ (M^{2+} = Ni, Ca, Mg, Mn, or Fe; M^{3+} = Fe, V, Ti, Cr, or Al). Roasting with sodium and/or calcium salts binds most vanadium ions into vanadates. Depending on the reagent proportions, air-stable vanadium bronzes where vanadium exists in the form of vanadium(V) and vanadium(IV) can exist together with vanadium(V) compounds in heat treated mixtures. Oxidative roasting with additives increases vanadium recovery by several times due to higher degrees of vanadium(V) recovery to aqueous solutions of acids and salts [1]. One task of this work was to study phase equilibria in the system including vanadium, calcium, sodium, and manganese oxides in the V₂O₅-NaVO₃-Ca(VO₃)₂-Mn₂V₂O₇ technologically significant region (with account for $Na_2Mn_3(V_2O_7)_2$) and to model the phase composition of a vanadium-containing feedstock containing considerable calcium and magnesium proportions and roasted with sodium salts additives. Another task was to determine vanadium recovery to sulfuric acid and sodium hydroxide solutions from phases of this system and their solid solutions.

Subsolidus phase relations in ternary subsystems are described in the literature. In the V_2O_5 -Ca(VO_3)₂- $Mn(VO_3)_2$ system (Fig. 1a), incomplete solid solutions are formed on the basis of calcium metavanadate $(Ca_{1-x}Mn_x(VO_3)_2 \text{ with } 0 \le x \le 0.62)$ and manganese metavanadate ($Mn_{1-x}Ca_x(VO_3)_2$ with ($0 \le x \le 0.32$) [2]. In the $Ca(VO_3)_2$ -NaVO₃ system, three phases were identified [3, 4]. One phase is an NaVO₃-base solid solution containing 0–5 mol % $Ca(VO_3)_2$. The second phase is the compound Na₂Ca(VO₃)₄, and the third is calcium metavanadate-base solid solution with solubility of 17 mol % NaVO₃. Figure 1b displays the triangulation of the V₂O₅-NaVO₃-Ca(VO₃)₂ system [3] with calcium account for sodium metavanadate Na₂Ca(VO₃)₄, NaVO₃- and Ca(VO₃)₂-base solid solutions, and two vanadium bronzes (Na_xV₂O₅ β -bronze with $0.22 \le x \le 0.40$ and $Na_{2+2x}V_6O_{16-y}$ κ -bronze with $0.25 \le x \le 0.45$ and $0 \le y \le 0.16$; for simplicity, the bronzes are arranged along the NaVO₃–V₂O₅ section as fixed compositions with their homogeneity ranges and vanadium(IV) ignored. The V_2O_5 -NaVO₃-Mn₂V₂O₇ system (with account for $Na_2Mn_3(V_2O_7)_2$) [5] is shown in Fig. 1c.

Sodium vanadates are water soluble [6]. Calcium vanadates are completely soluble at pH of 0.5–1.8; vanadium recovery to solution drops with increasing pH further, and does not increase considerably in the range of alkaline pHs [7]. β and κ sodium vanadium bronzes are almost insoluble when pH is 2–7; in ammo-



Fig. 1. Phase diagrams for (a) V_2O_5 -Ca(VO₃)₂-Mn(VO₃)₂, (b) V_2O_5 -Ca(VO₃)₂-NaVO₃, and (c) V_2O_5 -NaVO₃-Mn₂ V_2O_7 systems.

niac solutions, the dissolution rate of bronzes is a function of NH_3 concentration [8]. Studies of dissolution of manganese metavanadate, calcium metavanadate, and their solid solutions [9] showed that the increasing pH and manganese concentration decrease vanadium dissolution. However, solubility data are fragmentary; for double compounds, they are nonexistent. This gap is filled in by our study of the solubility of compounds formed in the title system and their solid solutions at pH of 1–10. Our data provide a basis for choosing optimal proportions of sodium-containing additives for generating the phase composition that determines maximal vanadium recovery during its leaching for subsequent selective sedimentation.

EXPERIMENTAL

Presynthesized sodium, calcium, and manganese vanadates were used as the starting components to prepare compounds and solid solutions of the V_2O_5 -NaVO₃-Ca(VO₃)₂-Mn₂V₂O₇ system. These vanadates were prepared by solid-phase sintering of V_2O_5 ,



Fig. 2. $NaVO_3$ - $Ca(VO_3)_2$ - $Mn(VO_3)_2$ section of the V_2O_5 - $NaVO_3$ - $Ca(VO_3)_2$ - $Mn_2V_2O_7$ quaternary diagram. For the compositions of samples 1–3, see the text.

Na₂CO₃, CaCO₃, and Mn₂O₃ mixtures (all high purity grade) at temperatures 20-30°C below the melting temperature of the mixture. Annealing lasted 10-50 h with intermittent grinding. X-ray powder diffraction analysis of products was carried out on a DRON-2 diffractometer (Cu K_{α} radiation); the JCPDS-ICDD database was used for phase identification. The behavior of vanadates in sulfuric acid and sodium hydroxide solutions with various pHs was studied using a routine procedure [1]: isothermal exposure of a test sample (<0.16 fraction) to solution for 10 min with constant stirring (1000 rpm); the ratio S/L = 1/1000. pH was adjusted by addition of the corresponding reagents and measured on a pH-673 ionometer/microvoltmeter. After the procedure was over, the residue was filtered and washed with water; the solution was analyzed for vanadium as in [10].

RESULTS AND DISCUSSION

To construct phase equilibrium diagrams for the title quaternary system, we used the phase composition of equilibrium samples synthesized from metavanadates $Ca(VO_3)_2$, $Mn(VO_3)_2$, and $NaVO_3$ determined in this work, along with the data on the ternary subsystems; this gave us the composition of secondary tetrahedra. The section of the V_2O_5 -Na₂O-CaO-MnO tetrahedron through the points corresponding to $Ca(VO_3)_2$, $Mn(VO_3)_2$, and $NaVO_3$, includes two quasi-binary systems: $Ca(VO_3)_2$ -NaVO₃ and $Ca(VO_3)_2$ Mn(VO₃)₂. The tie-line connecting Na_{2+2x}V₆O_{16-y} (κ) and $Na_2Mn_3(V_2O_7)_2$ passes through the secant plane on the $NaVO_3$ -Mn(VO_3)₂ side (Fig. 2). This uniquely determines the phase composition of the NaVO₃-

 $Ca(VO_3)_2$ -Mn(VO_3)_2 secant plane and, thus, elementary tetrahedra including metavanadates and the phase composition of heat-treated mixtures (550°C, 100 h):

$$0.3Na_2Ca(VO_3)_4 + 0.7Mn(VO_3)_2,$$
 (1)

$$0.5Na_2Ca(VO_3)_4 + 0.5Ca_{0.38}Mn_{0.62}(VO_3)_2, \qquad (2)$$

$$0.5Ca_{0.84}Na_{0.32}(VO_3)_2 + 0.5Ca_{0.38}Mn_{0.62}(VO_3)_2.$$
 (3)

After equilibration, the first sample was a mixture of NaVO₃, κ VB, Na₂Mn₃(V₂O₇)₂, and Ca_{0.38}Mn_{0.62}(VO₃)₂ phases. This determined the phase composition of the elementary tetrahedron whose corners are NaVO₃, the end-member of calcium metavanadate-base solid solution, and κ -VB. The plane of this elementary tetrahedron whose coordinates are the end-member of the calcium metavanadate-base solid solution, $Na_2Mn_3(V_2O_7)_2$, and κ -VB belongs to the neighboring tetrahedron whose fourth corner is the end-member of the calcium metavanadate-base solid solution $(Mn_{0.68}Ca_{0.32}(VO_3)_2)$. The existence of the plane in which $Na_2Mn_3(V_2O_7)_2$, κ -VB $Na_2 + 2xV_2O_{12}$, and $Mn_{0.68}Ca_{0.32}(VO_3)_2$ lie specified the corners of another elementary tetrahedron: Na₂Mn₃(V₂O₇)₂ K-VB Na_{2 +} $_{2r}V_2O_{12}$, and its edge (Mn_{1-r}Ca_r(VO₃)₂). Phase equilibria in the ternary subsystems give us the composition of elementary tetrahedra that include V_2O_5 and β -VB $Na_rV_2O_5$. The phase composition of heat-treated samples 2 and 3 validated the adequacy of the trends of tielines on the ternary subsystems in elementary tetrahedra. For example, the phase composition of sample 2 after annealing did not change, which gave rise to the $Na_2Ca(VO_3)_4$ – $Ca_{0.38}Mn_{0.62}(VO_3)_2$ equilibrium line, which lies in the metavanadate plane. The phase composition of annealed sample 3 revealed solid solution



Fig. 3. Phase diagram for the V₂O₅-NaVO₃-Ca(VO₃)₂-Mn₂V₂O₇ system.

 $Ca_{1-x-y}Mn_xNa_{2y}(VO_3)_2$ and an insignificant amount of $Na_2Ca(VO_3)_4$.

The above results were used to tetrahedrize the chosen fragment of the V_2O_5 -Na₂O-CaO-MnO system. The subsolidus phase diagram for the V_2O_5 -NaVO₃-Ca(VO₃)₂-Mn₂V₂O₇ system (including Na₂Mn₃(V₂O₇)₂) is broken into the following elementary tetrahedra:

(I) β -VB-V₂O₅-Mn_{1-x}Ca_x(VO₃)₂,

(II) β -VB-V₂O₅-Mn_{0.68}Ca_{0.32}(VO₃)₂-Ca_{0.38}Mn_{0.62} (VO₃)₂,

(III) β -VB-V₂O₅-Ca_{1-x}Mn_x(VO₃)₂,

(IV) β -VB- κ -VB-Mn_{1-x}Ca_x(VO₃)₂,

(V) β -VB- κ -VB-Mn_{0.68}Ca_{0.32}(VO₃)₂- Ca_{0.38}Mn_{0.62} (VO₃)₂,

(VI) β -VB- κ -VB-Ca_{1-x}Mn_x(VO₃)₂,

(VII) κ -VB–Na₂Mn₃(V₂O₇)₂–Mn_{1-x}Ca_x(VO₃)₂,

(VIII) $\kappa\text{-VB}-Na_2Mn_3(V_2O_7)_2-NaVO_3-Mn_{0.68}Ca_{0.32}$ (VO_3)2,

(IX) $\kappa\text{-VB-Na}_2Mn_3(V_2O_7)_2\text{-Ca}_{0.38}Mn_{0.62}(VO_3)_2\text{-Mn}_{0.68}$ Ca_{0.32}(VO_3)_2,

(X) κ -VB–Na₂Ca(VO₃)₄–Ca_{0.38}Mn_{0.62}(VO₃)₂–Na_{0.95} Ca_{0.025}VO,

 $(XI) \ \kappa \text{-VB-Na}_2 Ca(VO_3)_4 - Ca_{0.84} Na_{0.32} (VO_3)_2 - Ca_{0.38} Mn_{0.62} (VO_3)_2,$

(XII) κ -VB-Ca_{1-x-y}Mn_xNa_{2y}(VO₃)₂,

(XIII) κ -VB-Ca_{0.38}Mn_{0.62}(VO₃)₂-Na_{1-x}Ca_{0.5x}VO₃,

 $\begin{array}{l} (XIV) \quad \kappa \text{-VB}-Mn_2V_2O_7\mbox{-}Mn_{0.68}Ca_{0.32}(VO_3)_2\mbox{-}Ca_{0.38}\\ Mn_{0.62}(VO_3)_2\mbox{-}Na_2Mn_3(V_2O_7)_2, \end{array}$

(XV) κ -VB-Mn₂V₂O₇-Na₂Mn₃(V₂O₇)₂-Mn_{1 - x}Ca_x (VO₃)₂.

The tetrahedration of the quaternary system is displayed in Fig. 3. The above equilibrium system features two groups of vanadium compounds: vanadates with the maximal vanadium valence and vanadium bronzes containing partially reduced vanadium. In the first thirteen elementary tetrahedra, sodium vanadium bronzes coexist with their solid solutions. It is important for hydrometallurgical recovery of vanadium to account for the presence of vanadium bronzes in most compositions, because vanadium bronzes, unlike vanadates, are stable in acid media with pH higher than 1. Vanadium bronze generation upon equilibration can be avoided only in the region of compositions in the vicinity of manganese pyrovanadate (elementary tetrahedra XIV and XV).

Figures 4 and 5 plot vanadium recovery (α) curves at 20°C from calcium and manganese metavanadates, calcium and manganese pyrovanadates, their solid solutions, and the double compounds Na₂Ca(VO₃)₄ and NaMn₃(V₂O₇)₂, which form in the quaternary system



Fig. 4. Panel (a): vanadium recovery to solution vs. pH at 20°C for $Ca(VO_3)_2$ and its base solid solutions: (*1*) $Ca(VO_3)_2$, (2) $Ca_{0.75}Mn_{0.25}(VO_3)_2$, (3) $Ca_{0.38}Mn_{0.62}(VO_3)_2$ (4) $Ca_{0.84}Na_{0.32}(VO_3)_2$, and (5) $Na_2Ca(VO_3)_4$. Panel (b): the same for $Mn(VO_3)_2$ and its base solid solutions: (*1*) $Mn(VO_3)_2$, (2) $Mn_{0.85}Ca_{0.15}(VO_3)_2$, and (3) $Mn_{0.68}Ca_{0.32}$ (VO₃)₂.

under study. From samples with compositions in the region of $Ca_{1-x}Mn_xV_2O_6$ solid solution with x = 0.25 and 0.62, vanadium almost completely goes to solution during the experiment at pH of 0.5–2. With pH increasing to 3.5, α decreases regardless of manganese concentration. Vanadium dissolution at pH higher than 4 for these samples does not exceed 10%. Sodium for calcium substitution increases vanadium recovery compared to pure calcium metavanadate; even for this sample, however, α decreases monotonically at pH higher than 2; in aqueous solution, its value is 20%. Calcium sodium metavanadate Na₂Ca(VO₃)₄ is completely soluble when pH is within 0.5–9 (Fig. 4a). Calcium for manganese substitution in solid solution Mn_{1-x}Ca_xV₂O₆



Fig. 5. Panel (a): vanadium recovery to solution vs. pH at 20°C for $Mn_2V_2O_7$, its base solid solutions, and $Na_2Mn_3(V_2O_7)_2$: (1) $Mn_2V_2O_7$, (2) $Mn_{1.9}Ca_{0.1}V_2O_7$, (3) $Mn_{1.5}Ca_{0.5}V_2O_7$, (4) $MnCaV_2O_7$ and (5) $Na_2Mn_3(V_2O_7)_2$. Panel (b): the same for $Ca_2V_2O_7$ and its base solid solutions: (1) $Ca_2V_2O_7$ and (2) $(Ca_{0.75}Mn_{0.25})_2V_2O_7$.

increases vanadium recovery to solution for pH of 0.5 to 4; for both undoped and doped manganese metavanadate, however, vanadium concentration in sulfuric acid solution drops abruptly in this pH range. A rise in pH above 4 leaves vanadium recovery unchanged at a level of about 10% (Fig. 4b). Figure 5a displays vanadium recovery curves for manganese pyrovanadatebase solid solution samples. Manganese for calcium substitution until the composition is MnCaV₂O₇ strongly increases solubility when pH is 0.5–3. In neutral and alkali solutions, manganese pyrovanadate and its base solid solutions are almost insoluble. It is of interest to compare α for calcium pyrovanadate (Fig. 5b) and manganese pyrovanadate (Fig. 5a). In both cases, $\alpha = 100\%$ when pH is 0.5–3; as pH rises further, solubility drops. However, manganese for calcium substitution does not change vanadium recovery, unlike in manganese pyrovanadate-base solid solution. Figure 5a also displays α versus pH curves for manganese sodium pyrovanadate Mn₃Na(V₂O₇)₂. With pH rising from 0.5 to 3, α drops from 92 to 70%; with pH of 4 or higher, α remains unchanged and equals 30%.

Matching the vanadium recovery into solution from the phases of the V_2O_5 -NaVO₃-Ca(VO₃)₂-Mn₂V₂O₇ system to the compositions of elementary tetrahedra, we can a priori determine α for a phase mixture. The maximal vanadium recovery is determined by the absence of sodium vanadium bronze in the tetrahedron. This is possible for the sodium, calcium, and vanadium concentrations corresponding to the fragment of metavanadate plane confined to NaVO₃ and calcium metavanadate-based solid solution $Ca_{1-x}Mn_x(VO_3)_2$. Vanadium bronzes likewise do not form in the $Mn_2V_2O_7$ - $Mn_{0.68}Ca_{0.32}(VO_3)_2 - Ca_{0.38}Mn_{0.62}(VO_3)_2 - Na_2Mn_3(V_2O_7)_2$ and $Mn_2V_2O_7$ -Na₂Mn₃(V₂O₇)₂-Mn_{1-x}Ca_x(VO₃)₂ unit tetrahedra; at pH \leq 2, however, the maximal vanadium recovery is achievable in the absence of $Na_2Mn_3(V_2O_7)_2$ in the system.

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