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ABSTRACT

Alkaline hydrothermal solutions of sodium orthophosphate ($2.15 < \text{Na/P} < 2.75$) are shown to decompose transition metal oxides into two families of sodium-metal ion-(hydroxy)phosphate compounds. Equilibria for these reactions are quantified by determining phosphate concentration-temperature thresholds for decomposition of five oxides in the series: Ti(IV) , Cr(III) , Fe(III) , Ni(II) and Zn(II) . By application of a computational chemistry method General

Utility Lattice Progra

m (GULP), it is demonstrated that the unique non-whole-number Na/P molar ratio of sodium ferric hydroxyphosphate is a consequence of its open-cage structure in which the H^+ and excess Na^+ ions are located.

key words: transition metal oxides, hydrothermal reactions, sodium-iron(III)-hydroxyphosphate, sodium-chromium(III)-hydroxyphosphate, sodium-nickel(II)-hydroxyphosphate, maricite, sodium-zinc(II)-phosphate

INTRODUCTION

Sodium orthophosphate is a classical boiler water additive, whose original purpose was to precipitate 'hardness' ions (Ca^{2+} , Mg^{2+}) away from heat transfer surfaces where they could subsequently be removed by periodic blowdowns. In modern high pressure boilers hardness/contaminant ions are removed proactively, usually by employing ion exchange technology, in the feedwater circuit. However, sodium phosphate may still be maintained in boiler water to provide a buffered alkalinity necessary to minimize corrosion of boiler internals.

One of the most common methods to control alkalinity with sodium phosphate is by adjusting the sodium-to-phosphate (Na/P) molar ratio between control limits of 2.15 and 2.75. These control points take advantage of naturally-occurring phase boundaries in the $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ ternary (Refs. 1-3). The higher ratio corresponds to the composition of the stable phase of trisodium phosphate at elevated temperatures; the lower ratio corresponds an invariant point for disodium phosphate solubility/immiscibility at elevated temperatures. Thus, when the (sodium) phosphate solubility limit is exceeded by boiling in crevice and other flow-occluded areas, the remaining liquid will have a controlled alkalinity.

A shortcoming of this treatment philosophy, known as coordinated phosphate treatment (CPT), is that it does not account for chemical interactions between the materials of construction and concentrated sodium phosphate solutions that occur below the phosphate solubility limits. That is, the importance of $\text{MeO}^x\text{-Na}_2\text{O}-\text{P}_2\text{O}_5\text{-H}_2\text{O}$ quaternaries is neglected. In these cases, MeO^x refers to metal oxides which may be part of the corrosion oxide layer on heat transfer surfaces or metal oxides carried into the boiler from the feedwater circuit.

By means of chemical reaction studies conducted in our laboratory, threshold levels of sodium phosphate and temperature have been established for the decomposition of Fe_3O_4 (Refs. 4, 5),

NiO (Ref. 6), CrOOH (Ref. 7), TiO₂ (Ref. 8) and ZnO (Ref. 9) into sodium-metal ion-(hydroxy) phosphate compounds. These reactions were isolated in conjunction with our metal oxide solubility studies, in which phosphatocomplexes of the hydrolyzed metal ions were shown to be the dominant form of the soluble metal ion species in solution, cf. Ref. 10. Under these circumstances, metal oxide solubilities increased continuously with phosphate concentration and temperature. A sodium ion-induced precipitation reaction of a hydrolyzed metal ion phosphatocomplex occurred once a sodium phosphate concentration-temperature threshold limit was exceeded because the above solubility increases could not be sustained indefinitely. Conversely, precipitate redissolution would occur when solution conditions were maintained on the other side of the phase boundary.

The purpose of this paper is threefold: (1) to summarize the identities of the sodium phosphate induced metal oxide decomposition reactions/products, (2) to compare their phase boundaries/thermochemical properties and (3) to employ a computational chemistry method to verify that the extracted thermochemical properties are consistent with their crystal structures. The latter item was undertaken to explain the non-whole-number stoichiometry exhibited by sodium-ferric-hydroxyphosphate (SiHP).

DECOMPOSITION PRODUCTS AND PHASE BOUNDARIES

In general, the reaction threshold (i.e., phase boundary) for a given metal oxide was found to depend on total phosphate ion concentration, Na/P molar ratio and temperature. Figure 1 plots the phosphate concentration-temperature thresholds for the five metal oxides in 2.3 Na/P solutions and compares them to the expected solubility limit of sodium phosphate. Each of these boundaries is discussed below.

Titanium(IV) Oxide (Rutile)

In power plants equipped with titanium-tubed condensers, it may be possible for TiO_2 corrosion products to be transported to the boiler. The TiO_2 decomposition reaction is written

and represents the sodium ion induced precipitation of a diphosphatocomplex of the hydrolyzed $Ti(IV)$ ion.

Chromium(III) Oxide

Chromium is an alloying constituent in stainless steel, as well as nickel base NiCrFe alloys, used for boiler tubes/interals. As shown in our solubility study of chromium(III) oxide, eskolaite (Cr_2O_3), is unstable in water below the critical point, and partially hydrates to chromium(III) oxide hydroxide (γ - $CrOOH$). Its decomposition reaction in alkaline sodium phosphate solutions is

given by

Again, two phosphato ligands are complexed to each hydrolyzed $Cr(III)$ ion, and the precipitated sodium-chromium(III)-hydroxyphosphate compound contains a 2.0 Na/P molar ratio.

Iron(III, II) Oxide (Magnetite)

The tubes in fossil-fired boilers are predominately steel and possess a corrosion layer of magnetite. In addition, the low temperature condensate/feedwater circuit may contribute iron corrosion products in the form of iron(III) oxide hydroxides, goethite and lepidocrocite, that transform to magnetite in the boiler. The sodium phosphate-induced decomposition of magnetite is approximated by

In contrast to sodium-Ti(IV) or Cr(III)-hydroxyphosphate, sodium-Fe(III)-hydroxyphosphate (SIHP) contains $\text{Na/P} = 2.15 \pm 0.02$, rather than 2.0. Replacing the magnetite reactant with hematite ($\alpha\text{-Fe}_2\text{O}_3$) has no effect on reaction product stoichiometry. Since the magnetite reaction involves the precipitation of the diphasatocomplex of the hydrolyzed Fe(III) ion, it is seen that dissolved hydrogen also plays a role in determining the phase boundary.

As shown by Bridson et al. (Ref. 11), the above representation of SIHP is an approximation,

since subsequent, precise single crystal X-ray diffraction analysis has revealed the true

molecular formula for SIHP to be $\text{Na}_3\text{Fe}(\text{PO}_4)_2 \cdot x\text{NaOH} \cdot x\text{H}_2\text{O}$, where $x = 2/3$. The compound is

orthorhombic, belonging to the space group *Ibam* (#72), and containing two partially occupied

lattice sites, i.e., H_x and Na_{1-x} . Since powder X-ray diffraction analyses of sodium-Cr(III)-

hydroxyphosphate (SCrHP) reveal it to be isostructural with SIHP, but chemical analyses

indicate whole number stoichiometry, we conclude that SCrHP does not exhibit partial site

occupancy, and has $x = 1$. The larger size of the Fe^{3+} ion relative to the Cr^{3+} ion is believed to

create a phosphate lattice having a larger open-cage structure which is capable of

accommodating larger Na^+ ions as well as H^+ ions.

Off-nominal Na/P ratios, caused by deliberate additions of monosodium phosphate (NaH_2PO_4),

or maintenance of Na/P molar ratios ≤ 2 , may allow a second iron oxide decomposition reaction

to occur:

The product occurs in nature as the mineral maricite, and possesses an orthorhombic crystalline lattice. The actual phase boundary should be written for a hydrous Fe(II) oxide reactant, rather than magnetite, since magnetite was unstable in the hydrogenated solutions investigated.

Nickel(II) Oxide (Bunsenite)

Nickel-base alloys are used in the boiler tubing of pressurized water reactors (PWRs); nickel may also be present in copper-nickel alloys used in condenser tubing. Bunsenite is decomposed by alkaline sodium phosphate solutions via

The existence of this phase boundary is especially significant, since decomposition of the

normally-protective metal oxide on nickel-base alloys becomes possible in flow-occluded zones (within tube supports and sludged regions). This occurrence represents the sodium phosphate-induced wastage phenomenon observed in PWR steam generators.

Additional results, obtained by reacting bunsenite in disodium phosphate solutions, revealed a

second route for decomposition:

Reaction product identity was verified by matching its X-ray diffraction pattern with that reported for $NaNiPO_4$ by Kolsi (Ref. 12).

Zinc(II) Oxide (Zincite)

Zinc may be present as a constituent in certain copper-base alloys used for condenser tubing and as a pigment in preservative coatings applied to reserve feedwater storage tanks. Its

decomposition reaction in hydrothermal alkaline sodium phosphate solutions is given by

Although the powder X-ray diffraction pattern for sodium zinc phosphate has been indexed to an orthorhombic lattice, $NaZnPO_4$ is isostructural with berylionite ($NaBePO_4$) rather than maricite ($NaFePO_4$). The symmetry of its lattice is actually monoclinic in which $\beta \approx 90^\circ$. The space

group for $NaZnPO_4$ and $NaBePO_4$ is $P2_1/n$ (#14) while $NaFePO_4$ is $Pnma$ (#62). This difference

is caused by tetrahedral coordination of Zn(II) and Be(II) with oxygen vs. octahedral coordination exhibited by Fe(II).

As solution Na/P ratios are lowered to ≤ 2.1 the phosphate ion hydrolytic equilibria are shifted to create sufficient concentrations of the $H_3PO_4(aq)$ species which may decompose zincite via a second route:

The product has the mineral name tarbutite. It is noteworthy that the reaction product is sodium-free, which tends to increase solution Na/P ratios in the vicinity of the decomposing ZnO so that decomposition ceases or is shifted to favor $NaZnPO_4$ formation.

THERMODYNAMIC ANALYSIS

In order to quantitatively model the expected regions of metal oxide stability in terms of total phosphate ion concentration, solution Na/P molar ratio and temperature, the equilibria for the isolated decomposition reactions must be made available. This task is accomplished by converting the measured thresholds at which decomposition is initiated into equilibrium constants, thereby defining Gibbs energy changes for the decomposition reactions via

$$\Delta G^\circ = -RT \ln K_{eq}$$

This analysis not only incorporates the Na/P ratio dependency, but allows thermochemical properties for the reaction products to be extracted for comparison/verification by other methods.

A summary of Gibbs energy changes for the metal oxide decomposition reactions, taken from our previous papers, is plotted in Fig. 2. Due to solution ionic strengths in the range 0.3 to 2.7, appreciable corrections were required to convert ionic concentrations to thermodynamic

activities. Also, because the equilibrium constants were obtained at elevated temperatures over relatively small ranges, extrapolation to 298.15 K (the usual reference state) is made highly uncertain.

To improve upon our previous estimates, which were based on linear correlations of ΔG° with temperature, we now invoke the isocoulombic principle (Ref. 13). This methodology is based on the observation that most aqueous phase reactions exhibit a linear $\Delta G(T)$ behavior only when written in a form that balances like ionic charges between reactants and products. For example, the rutile decomposition reaction may be placed in isocoulombic form by addition of equilibria for two stepwise hydrolysis reactions of the phosphate ion:

Upon summation, it is determined that $\Delta C_p^\circ \approx 696 \text{ J mol}^{-1} \text{ K}^{-1}$ for the rutile decomposition reaction.

Consistent with the approximate nature of the isocoulombic correction, ΔC_p° is assumed to be independent of temperature, which allows $\Delta G^\circ(T)$ to be expressed as

$$\Delta G^\circ(T) = A - BT - CT \ln T$$

The fitted constants have the thermodynamic significance $C = \Delta C_p^\circ$, $A = \Delta H^\circ(298) - 298.15 \Delta C_p^\circ$ and $B = \Delta S^\circ(298) - (1 + \ln 298.15) \Delta C_p^\circ$. Results of the refitted ΔG° database are summarized in Table I.

THERMOCHEMICAL PROPERTIES FROM CRYSTAL STRUCTURE VIA GULP

In anticipation of applying computational chemistry, detailed structural information was obtained for the reaction products by X-ray diffraction. By indexing the X-ray diffraction pattern, crystal symmetry and space group were established. Hence, positions of the individual atoms within a unit cell of the crystalline lattice became known, see Refs. (11, 15, 16). Using this information as input, the GULP code (General Utility Lattice Program) was applied to compute values of standard molar entropy and heat capacity for maricite, NaZnPO_4 , SIHP and SCRHP.

GULP is a public domain energy minimization program for solids (Ref.17), which was recently upgraded to permit evaluation of lattice vibrations where partial site occupancy exists. Interatomic energetics are modeled using a sum of short-range repulsion (Buckingham potential) and long-range electrostatic attraction:

$$E_{ij} = A \exp \{-r_{ij}/\rho\} - Cr_{ij}^{-6} + q_1q_2/r_{ij}$$

while the shell model (Ref. 18) is included to simulate polarization/covalency effects. The intrionic model employs a massless shell, on which all short-range forces act, and which is harmonically-coupled to a core from which it is coulombically screened:

$$E^{c-s} = (1/2) k(r_{c-s})^2$$

where k is the core-shell spring constant. All model parameters, summarized in Tables II and III, are considered optimal based on current literature. In order to model the O-H bond more accurately, a Morse (rather than Buckingham) potential was used:

$$E_m = D \left\{ 1 - \exp \left[-a(r_{ij} - r_o) \right] \right\}^2$$

Recommended values for the parameters, $D = 7.0525 \text{ eV}$, $a = 2.1986 \text{ \AA}^{-1}$ and $r_o = 0.9485 \text{ \AA}$, were taken from Ref. 23.

Given a starting geometry based on atom positions determined by XRD, GULP calculates total energy (sum of all E_{ij} and E_{cs} contributions) and the first and second derivatives with respect to position. If geometric convergence criteria are met, the program stops; otherwise new atom coordinates are generated based on the gradients calculated, and the total energy/derivatives are recalculated until convergence is obtained. The minimization was conducted at constant volume, where the unit cell dimensions remained fixed.

The second derivative matrix, F , is especially useful because its solution provides information on the vibrational modes and their frequencies:

$$(M^{-1}F - \lambda I)\psi = 0$$

Here M is the mass matrix of the system, and I is the unit matrix. The resulting eigenvectors (ψ) and eigenvalues (λ) allow calculation of the vibrational partition function (Q), from which S° and C_v° are determined

$$S = R \ln Q + RT \left(\frac{\partial}{\partial T} \ln Q \right)_v$$

$$C_v = T \left(\frac{\partial S}{\partial T} \right)_v$$

The standard molar entropies and heat capacities determined in this manner are given in Table IV and compared to values extracted from the Table I equilibria using compiled thermochemical properties for the reactants. Accuracies of the GULP-predicted thermochemical properties were estimated from the standard deviation between predicted and observed vibrational frequencies (based on infrared and Raman spectra, not shown) and a sensitivity analysis which revealed that a 1% change in vibrational frequency caused an ~0.5% change in S° and a 1% change in C_v . In this manner, the expected accuracies of S° and C_v for SIHP are 1% and 2%, respectively; those for SCrHP are 2.5% and 5%, respectively. The estimated C_p° values for maricite and SIHP differ by <1% and 5%, respectively, compared to calorimetric measurements

(Ref. 24). Due to this encouraging result, additional GULP calculations were performed with SIHP, varying the distribution between Na^+ and H^+ ions in the partially-occupied sites. The effect of composition changes in the partially-occupied Na(6) and H(1) sites was investigated by varying x between 0 and 1 and following changes in the calculated XRD pattern versus the experimental powder XRD pattern for SIHP. Mean squares residuals, as summarized in Table V, show a broad minimum for x between 0.45 and 0.65. The actual minimum occurs around $x \approx 0.65$, which differs by <3% compared to $x = 2/3$ found by quantitative chemical analysis of SIHP. Therefore, the 'optimum' occupancy for SIHP predicted by GULP agrees with that measured by chemical means.

SUMMARY AND CONCLUSIONS

Alkaline hydrothermal solutions of sodium phosphate are shown to decompose metal oxides into sodium-metal ion-(hydroxy)phosphate compounds. The identity of these compounds is established in solutions having Na/P molar ratios typical of those maintained by coordinated phosphate treatment (CPT). All reaction products contain sodium and phosphate in whole number ratios (i.e., 2, 1, or 0), except for SIHP. Although the SIHP and SCrHP precipitates have similar, cage-like crystalline lattices in which the H^+ ion is located, the larger size of the Fe^{3+} ion relative to Cr^{3+} produces a larger 'cage' that can accommodate excess Na^+ ions as well. Therefore, SIHP possesses a unique 2.17 Na/P molar ratio.

Our study has shown that CPT philosophy, which relies on phase boundaries in the $\text{Na}_2\text{O-P}_2\text{O}_5\text{-H}_2\text{O}$ ternary to control boiler water alkalinity in flow-occluded regions, is flawed due to the presence of phase boundaries in various $\text{MeO}_x\text{-Na}_2\text{O-P}_2\text{O}_5\text{-H}_2\text{O}$ quaternaries. Such behavior has led to a second boiler water treatment philosophy, known as equilibrium phosphate treatment (EPT), Ref. 25. By forcing operation with $\text{Na/P} > 2.8$, the iron oxide decomposition

reaction is prevented, since the $\text{Na}_2\text{O-P}_2\text{O}_5\text{-H}_2\text{O}$ phase boundary (i.e., phosphate solubility limit) is shifted below the iron oxide- $\text{Na}_2\text{O-P}_2\text{O}_5\text{-H}_2\text{O}$ phase boundary. In order to compensate for the reduced phosphate solubility limits, however, bulk phosphate levels are maintained much lower than in CPT (< 2.5 ppm in EPT vs. 3-10 ppm in CPT). EPT is not without risk, however, since phase boundaries in $\text{MeO}_x\text{-Na}_2\text{O-H}_2\text{O}$ ternaries need to be considered.

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REFERENCES

1. D. Broadbent, G. G. Lewis and E. A. M. Wetton, *J. Chem. Soc. Dalton* (1977) 464-468
2. P. Taylor, P. R. Tremaine and M. G. Bailey, *Inorganic Chem.* 18 (1979) 2947
3. E. A. M. Wetton, *Power Industry Res.* 1 (1981) 151-158
4. S. E. Ziemniak and E. P. Opalka, *Proc. Sixth International Symposium on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors* (1993) 929-935
5. S. E. Ziemniak and H. M. Tunison, *PPChem.* 5 (2003) 69-74
6. S. E. Ziemniak and E. P. Opalka, *Proc. Third International Symposium on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors* (1988) 153
7. S. E. Ziemniak and E. P. Opalka (in review) (Phase Stability of Chromium Oxide Hydroxide in Alkaline Sodium Phosphate Solutions)
8. S. E. Ziemniak and E. P. Opalka, *Chem. Mater.* 5 (1993) 690-694
9. S. E. Ziemniak and E. P. Opalka, *Chem. Mater.* 6 (1994) 461-467
10. S. E. Ziemniak, M. E. Jones and K. E. S. Combs, *J. Solution Chem.* 22 (1993) 601-623
11. J. N. Bridson, S. E. Quinlan and P. R. Tremaine, *Chem. Mater.* 10 (1998) 763-768
12. A.-W. Kolsi, *Rev. Chim. Minerale* 16 (1979) 593-596

13. R. E. Mesmer, W. L. Marshall, D. A. Palmer, J. M. Simonson and H. F. Holmes, *J. Solution Chem.* 21 (1988) 699
- J. W. Larson, K. G. Zeib and L. G. Hepler, *Can. J. Chem.* 60 (1982) 214.
15. Y. LePage and G. Donnay, *Can. Mineralogist* 15 (1977) 518-521
16. N. I. Golovastikov, *Soviet Phys. - Crystallography* 6 (1962) 733-739
17. J. D. Gale, *J. Chem. Soc. Faraday Trans. 93* (1997) 629-637
- B. G. Dick and A. W. Overhauser, *Phys. Rev.* 112 (1958) 90
19. C. R. A. Catlow, *Proc. Royal Soc. London A355* (1977) 533
20. R. A. Jackson and C. R. A. Catlow, *Molecular Simulation* 1 (1988) 207-224
21. J. D. Gale and N. J. Henson, *J. Chem. Soc. Faraday Trans. 90* (1994) 3175-3179
22. G. V. Lewis and C. R. A. Catlow, *J. Phys.* 18C (1985) 1149-1161
23. K.-P. Schröder, J. Sauer, M. Leslie, C. R. A. Catlow and J. M. Thomas, *Chem. Phys. Lett.* 188 (1992) 320-325
24. P. R. Tremaine and C. Xiao, *J. Chem. Thermodynamics* 31 (1999) 1307-1320
25. J. Stodola, *PPChem.* 5 (2003) 75-84

Table
Free Energy Changes for Metal Oxide Decomposition Reactions
in Hydrothermal Alkaline Sodium Phosphate Solutions

Reaction	A kJ mol ⁻¹	B J mol ⁻¹ K ⁻¹	C* J mol ⁻¹ K ⁻¹	ΔG°(298) kJ mol ⁻¹
TiO ₂ (s) + 4Na ⁺ + 2HPO ₄ ²⁻ = Na ₄ Ti(OH) ₂ (PO ₄) ₂ (s)	-66.26±9.33	-4362.3±17.8	696	52.04
CrOOH(s) + 4Na ⁺ + 2HPO ₄ ²⁻ = Na ₄ Cr(OH)(PO ₄) ₂ (s) + H ₂ O	158.96±50.80	-3970.0±93.52	696	160.29
1/3 Fe ₃ O ₄ (s) + 13/3 Na ⁺ + 2HPO ₄ ²⁻ = Na ₃ Fe(PO ₄) ₂ ·NaO(Na _{1/3} H _{2/3})(s) + 1/3H ₂ O + 1/3H ⁺ + 1/6H ₂ (g)	-80.70±6.59	-4451.3±12.7	696	64.13
Fe(OH) ₂ (s) + Na ⁺ + H ₂ PO ₄ ⁻ = NaFePO ₄ (s) + 2H ₂ O	-29.65±6.39	-811.4±13.1	128	-5.18
NiO(s) + 2Na ⁺ + HPO ₄ ²⁻ = Na ₂ Ni(OH)PO ₄ (s)	37.21±8.52	-2071.0±15.6	348	63.51
NiO(s) + Na ⁺ + H ₂ PO ₄ ⁻ = NaNiPO ₄ (s) + H ₂ O		**	128	
ZnO(s) + Na ⁺ + H ₂ PO ₄ ⁻ = NaZnPO ₄ (s)	-62.26±5.53	-815.6±12.6	128	-36.53
2ZnO(s) + H ₃ PO ₄ = Zn ₂ (OH)(PO ₄) ₂ (s) + H ₂ O	-27.64±1.70	-98.44±3.39	0	-56.99

* Value constrained by isocoulombic analysis, see text.

** Insufficient data; only one value known: ΔG°(539) = 26.79 kJ mol⁻¹

Table II

Short-range interionic potential model parameters*

Ion Pair	A (eV)	ρ (Å)	C (eV Å ⁶)
Na _s - Na _s	7895.4	0.1709	
Na _s - O _s	1226.84	0.3065	
P _c - O _s	877.34	0.3594	
Zn _s - O _s	499.6	0.3595	
Fe(II) _s - O _s	694.1	0.3399	
Fe(III) _s - O _s	1102.4	0.3299	
Cr _s - O _s	1734.1	0.3010	
O _s - O _s	22764.0	0.149	27.88
H _s - O _s		(see text)	

$$* E_{ij} = A \exp(-r_{ij}/\rho) - C/r_{ij}^6$$

Intralaionic charges and spring constants used in GULP*			
Ion	Core Charge	Shell Charge	Spring Constant, $\text{ev \AA}^{-2}$
Na	-1.13	2.13	96.44
Zn	-0.05	2.05	10.28
Fe(II)	0.0	2.00	
Fe(III)	-1.97	4.97	304.7
Cr	2.03	0.97	
P	5.0	0.0	
O	0.86	-2.86	

* From Refs. (20, 22).

Table III

Table IV

Comparison of experimentally determined thermochemical properties for sodium-metal ion(hydroxy)phosphate compounds with GULP predictions

Compound	$C_p^{(298)}$ J mol ⁻¹ K ⁻¹	$S^\circ(298)$ J mol ⁻¹ K ⁻¹	$\Delta H_f^\circ(298)$ kJ mol ⁻¹	$\Delta G_f^\circ(298)$ kJ mol ⁻¹	Source
Na ₄ Ti(OH) ₂ (PO ₄) ₂	428	432.7	-4374.98	-4064.50	Table
Na ₄ Cr(OH)(PO ₄) ₂		815.4	-3641.28	-3497.01	Table
	270*	256			GULP
SIHP (x = 2/3)	409	316.0	-3802.22	-3509.58	Table
	301*	293			GULP
	285.9				Ref. 24
NaFePO ₄		99.0	-1552.14	-1423.76	Table
	124*	112			GULP
	123.3				Ref. 24
Na ₂ Ni(OH)PO ₄	231	339.3	-1884.47	-1761.55	Table
NaZnPO ₄	105	124.6	-1638.00	-1512.96	Table
	128*	148			GULP

*Predicted C_v value converted to C_p° using relationship $C_p^\circ - C_v \approx 0.5\% C_v$

Table V

Effect of (excess) sodium ion content in SIHP on XRD pattern
residuals calculated by GULP

H(1) Site Occupancy, x*	Na/P in SIHP	XRD Pattern Residual
0.0	2.50	0.6688
0.1	2.45	0.6618
0.2	2.40	0.6562
0.3	2.35	0.6507
0.4	2.30	0.6471
0.452	2.274	0.6468
0.5	2.25	0.6464
0.6	2.20	0.6462
0.667	2.167	0.6478
0.7	2.15	0.6487
0.75	2.125	0.6505
0.8	2.10	0.6537
0.9	2.05	0.6633
1.0	2.00	0.6737

Occupancy of Na(6) site is 1-x.

Fig. 1 Comparison of reaction thresholds for metal oxide decomposition vs. sodium phosphate solubility limit (in 2.3 Na/P solutions, unless noted otherwise).

Fig. 2. Free energy changes determined for metal oxide decomposition reactions in

hydrothermal alkaline sodium phosphate solutions: (a) CrOOH/SCrHP , (b)

$\text{NiO}/\text{Na}_2\text{Ni}(\text{OH})\text{PO}_4$, (c) $\text{Fe}_3\text{O}_4/\text{SiHP}$, (d) $\text{TiO}_2/\text{Na}_4\text{Ti}(\text{OH})_2(\text{PO}_4)_2$, (e)

$\text{Fe}_3\text{O}_4/\text{NaFePO}_4$ and (f) $\text{ZnO}/\text{NaZnPO}_4$.