Phase Stability of Chromium(III) Oxide Hydroxide in Alkaline Sodium Phosphate Solutions

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ABSTRACT

Grimaldiite (α-CrOOH) is shown to transform to a sodium-chromium(III)-hydroxyphosphate compound (SCHP) in alkaline sodium phosphate solutions at elevated temperatures via

$$CrOOH(s) + 4Na^+ + 2HPO_4^{2-} = Na_4Cr(OH)(PO_4)_2(s) + H_2O$$
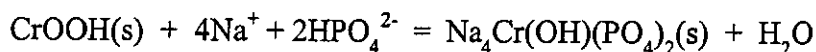
X-ray diffraction analyses indicate that SCHP possesses an orthorhombic lattice having the same space group symmetry (Ibam, #72) as sodium ferric hydroxyphosphate. A structurally-consistent designation for SCHP is $Na_3Cr(PO_4)_2 \cdot NaOH$; the molar volume of SCHP is estimated to be 1552 cm^3. The thermodynamic equilibrium for the above reaction was defined in the system Na_2O-P_2O_5-Cr_2O_3-H_2O for Na/P molar ratios between 2.0 and 2.4. On the basis of observed reaction threshold values for sodium phosphate concentration and temperature, the standard molar entropy (S^o), heat capacity (C_p^o) and free energy of formation (ΔG_f^o) for SCHP were calculated to be 690 J/(mol-K), 622 J/(mol-K) and -3509.97 kJ/mol, respectively.

PHASE STABILITY OF CHROMIUM(III) OXIDE HYDROXIDE IN ALKALINE SODIUM PHOSPHATE SOLUTIONS AT ELEVATED TEMPERATURES

INTRODUCTION

The phase stability of chromium(III) oxides has important implications regarding the

degradation of NiCrFe alloys in high temperature aqueous systems, since the 'protective'

corrosion oxide films that form on such materials are Cr(III) based.[1] A recent solubility study

of chromium(III) oxide (eskolaite) in alkaline sodium phosphate solutions[2] determined that

chromium(III) oxide hydroxide, rather than Cr_2O_3, was thermodynamically stable at

temperatures above 55°C and that for phosphate concentrations greater than 0.1 mol/kg, the

dissolution reaction equilibrium was controlled by formation of anionic hydroxophosphato-

complexes of the Cr(III) ion. Under these conditions, Cr(III) ion solubilities increased with

phosphate concentration and temperature. By analogy with the behavior of other transition metal

oxides,[3,4] it is expected that such solubility increases cannot be sustained indefinitely, and that

once certain threshold levels of sodium, phosphate and temperature are reached, a sodium ion-

induced precipitation reaction will occur.

The purposes of the present investigation are to determine: (1) the identity of the

precipitated phase and (2) the threshold conditions required for its formation. The information

collected is then used to derive thermodynamic properties for the precipitated phase.

EXPERIMENTAL

Autoclave Tests

Ten tests were conducted in a one-liter, gold-lined autoclave vessel fitted with a platinum

'dip' tube to permit hot sampling. A sketch of the apparatus is shown in Fig. 1. The

experimental methodology used was the same as that described in previous reaction studies with

NiO,[5] Fe_3O_4,[3] TiO_2[4] and ZnO[6]. This methodology consisted of incrementally elevating the

temperature of a concentrated sodium phosphate solution in the presence of a CrOOH powder (4 – 5 g) reactant until a phosphate loss is observed. One test (2A) used a 3 g charge of CrOOH.

Reagents

Chromium(III) oxide hydroxide (α-CrOOH) was prepared by hydrothermal dehydration of a chromium(III) hydroxide intermediate, which had been precipitated from $CrCl_3$ solutions at room temperature with excess ammonia. The chromium(III) hydroxide precipitate had been rinsed with deionized water until no detectable chloride remained in solution. The precipitate was also oven dried at 54°C for 24 hours. The $Cr(OH)_3$ powder was then transformed hydrothermally into CrOOH by autoclaving in dilute, alkaline sodium phosphate solutions (3 mmol/kg). The material was processed in three batches:

Batch	Amount	Temp.	Time	Where Tested
1	15 g	300°C	3 days	1, 2A, 3, 5
2	10 g	300°C	5 days	4, 6
3	15 g	315°C	4 days	2, 7, 8, 9

All three batches produced material that was blue-green in color and exhibited an XRD pattern characteristic of α-CrOOH (grimaldiite, JCPDS 33-600).[7] Based on XRD line broadening, it is estimated that the average crystal sizes were 300, 50 and 100 Å, for the respective batches 1 – 3.

All sodium phosphate solutions were prepared using analytical or equivalent grade Na_2HPO_4 (anhyd.) and $Na_3PO_4 \cdot 12H_2O$ obtained from the Fisher Scientific Company.

Analytical Procedures

The total phosphate concentration of each sample aliquot was determined by a standard potentiometric-titration procedure in which a known sample volume was diluted and titrated with

0.100$\underline{N}$ HCl. The amount of titrant used between pH 9.2 ± 0.1 (x) and 5.0 ± 0.1 (y), i.e.,

inflection points corresponding to orthophosphate ionization equilibria, was taken to be the

equivalent amount of phosphate. Solution density corrections were applied to convert to

molality units.

The sodium-to-phosphate molar ratio (Na/P) was then calculated by Na/P = (2y – x)/(y –

x). The estimated precision in Na/P is calculated to be ± 0.003 given a standard burette reading

accuracy of ± 0.02 ml and typical values of x and y (3, 13 ml).

Upon completion of each autoclave experiment, the platinum holder containing the

reacted CrOOH powder was rinsed with deionized water and subjected to visual examination

under a stereomicroscope. A portion of the reaction cake was then fractured and placed on a

mount for high magnification viewing on a scanning electron microscope. By means of micro-

manipulators, i.e., needles and tweezers, crystals of the reaction products were separated from

the remaining mass of unreacted/reacted material. Samples isolated in this manner were

subjected to X-ray diffraction (XRD) analyses. Powder XRD measurements were performed

using a Model CN2155D5 Rigaku diffractometer (Bragg-Brentano geometry) and CuK$_{\alpha}$

radiation (λ = 1.5417 Å). The X-ray tube was operated at 45 kV and 20 ma. Data were taken as

a continuous scan from 8 to 92 deg. (2θ) at a speed of 1 deg. min^{-1}.

To further aid reaction product characterization, two additional analyses were performed

on the 'purified' reaction product crystals from Test 6: infrared absorption (KBr pellet technique)

and quantitative (wet) chemical.

RESULTS

Chromium(III) Oxide Hydroxide Phase Boundary

Threshold temperatures at which sodium phosphate precipitation was initiated, were

determined by reverse extrapolation of phosphate versus temperature plots. At least three

temperature points above the threshold level were included from each run. Based on changes in

the Na/P ratios of the depleted test solutions, compared with initial (baseline) values, indicated Na/P loss ratios were calculated. These values, along with the estimated CrOOH transformation temperatures are summarized in Table I.

Based on the above ten tests, CrOOH transforms into a compound having a Na/P molar ratio equal to 2.0/1.

Characterization of Precipitated Phase

The reaction products, when viewed under the stereomicroscope at 50X, were pale green-blue in color. Although the individual crystals were very small, their presence was discernable by the 'sparkle' produced by light reflection. Fig. 2 shows a representative collection of SEM photographs taken of the reaction product crystals from Tests 4 and 6 at magnifications between 1000 and 2000X. These photographs reveal the reaction product crystals to have a flattened, whisker-like appearance. In many instances the whiskers had grown into slabs or laths. Semiquantitative EDX microprobe analyses, performed with the SEM, consistently showed that sodium, phosphorus and chromium were the major elements present in the crystals.

X-ray diffraction analyses revealed that the reaction products from all ten runs had an identical crystalline lattice configuration. The powder XRD pattern for the reaction product is compared to that previously obtained for sodium ferric hydroxyphosphate (SIHP) in Table II. Due to their similarity, it is concluded that both compounds possess the same crystal structure, i.e., are orthorhombic and have the space group Ibam (#72), see Reference (8). The reaction product is seen to have smaller unit cell dimensions than SIHP, a result consistent with the smaller size of the Cr^{3+} ion relative to Fe^{3+} (i.e., 0.615 vs. 0.645 Å):[9]

Unit Cell Lattice Parameters, Å

Reaction Product	a	b	c
SCHP	14.524	15.451	7.156
SIHP, [3]	14.618	15.436	7.122
SIHP, [8]	14.698	15.522	7.114

The presence of the hydroxide ion was confirmed by infrared analysis of the Test 1 and 6 reaction products. Absorption in the vicinity of 3500 cm^{-1}, which represents the stretching frequency of the O-H bond, confirms the presence of the hydroxyl group. The hydroxide ion absorption band, however, is shifted to a lower frequency (3530 vs. 3550 cm^{-1}) relative to SIHP. Furthermore, the hydroxide ion stretching is simpler in the chromium compound, since the additional band observed at 3580 cm^{-1} in SIHP is absent.

Quantitative energy dispersive X-ray (EDX) analyses of twelve randomly selected crystals from Test 6 were performed using a Noran MicroZ thin window X-ray detector attachment to a Phillips Model EM420 analytical electron microscope. The Cr/P atom ratio of the reaction products was found to have a mean value of 0.51 ± 0.05. An additional electron microprobe analysis (wavelength dispersive) of the Test 6 reaction product, based on calibrations relative to sodium phosphate reference standards (and including corrections for intermetallic effects), gave a Na/P atom ratio of 1.9 ± 10%. This value compares very well with the 2.0 Na/P ratio inferred from the autoclave test solution losses summarized in Table 1.

Assembly of the above information gives $Na_4Cr(OH)(PO_4)_2$ as the lowest whole number stoichiometry for sodium-chromium-hydroxyphosphate (SCHP). Its indicated composition, by weight percentages, is: 26.2 Na, 14.8 Cr, 54.1 PO_4 and 4.8 OH. Quantitative wet chemistry results for the 'purified' Test 6 reaction product proved inconclusive, since increased levels of Cr relative to Na and P were found, consistent with a 15% CrOOH contamination level in SCHP.

However, the 2.0 Na/P ratio was verified. Based on the measured unit cell dimensions of SCHP, it is calculated that $V^{\circ}(298) = 1552$ cm^3/mol.

DISCUSSION OF RESULTS

Stoichiometry of Sodium Chromic Hydroxyphosphate

The sodium phosphate-induced decomposition of chromium(III) oxide (hydroxide) in high temperature aqueous solutions leads to the formation of $Na_4Cr(OH)(PO_4)_2$. This compound has an integer ratio of 2 for Na/P, consistent with the decomposition products observed for two other transition metal oxides: $NiO - Na_2Ni(OH)PO_4$[5] and $TiO_2 - Na_4Ti(OH)_2(PO_4)_2$.[4] This observation indicates that the results of Fe(III) oxide (or Fe_3O_4) decomposition (the only other trivalent transition metal oxide investigated to date) are an exception to the integer stoichiometry.

Recent, single-crystal X-ray diffraction studies of SIHP have determined individual atom positions which indicate the structural formula as $Na_3Fe(PO_4)_2 \cdot NaO(H_xNa_{1-x})$.[8] The unique feature of this lattice structure is that the 'excess' Na_{1-x} and H_x sites appear at different locations, although their total site occupancy sums to unity. Our previous results suggest that $x = 2/3$,[3] while Tremaine et al.[8] suggest $x = 0.45$. Our present results conclusively demonstrate that x is unity in SCHP and that the above partial site occupancy phenomenon does not exist for SCHP.

It is also reassuring that the observed P/Cr atom ratio of SCHP has an integer value of 2. This value is consistent with the presence in solution of a Cr(III) ion diphosphato-complex, previously reported to control the solubility behavior of CrOOH in alkaline sodium phosphate solutions at elevated temperatures.[2] The subsequent sodium ion-induced precipitation reaction is believed to expel three water molecules, i.e.,

$$4Na^+ + Cr(OH)_4(HPO_4)(H_2PO_4)^{4-} = Na_4Cr(OH)(PO_4)_2(s) + 3H_2O \qquad (1)$$
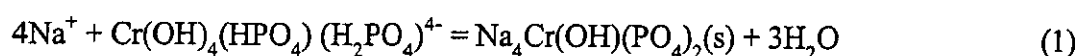
Thermodynamic Properties of SCHP

An overall transformation reaction, based on the identities of the solid phases present and written per mole of reaction product, is:

$$CrOOH(s) + 4Na^+ + 2HPO_4^{2-} = Na_4Cr(OH)(PO_4)_2(s) + H_2O \qquad (2)$$
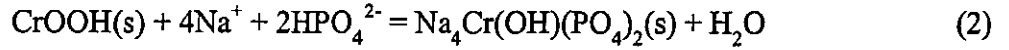
The equilibrium constant for Eq. (2) is defined by

$$K_{eq} = \frac{a_{Na_4Cr(OH)(PO_4)_2} a_{H_2O}}{a_{CrOOH} a_{Na^+}^4 a_{HPO_4^{2-}}^2} \qquad (3)$$

In the usual manner, activities (a_i) of water and the two solid phases were taken to be unity, whereas ionic activity coefficients (γ_i) were used to relate ionic concentrations (C_i) in molality units to thermodynamic activities. Marshall and Jones [10] show that an extended Debye-Hückel equation of the form

$$\log \gamma_i = -SZ_i^2 \sqrt{I} / (1 + 1.75 \sqrt{I}) \qquad (4)$$

with A = 1.75 gives reasonable approximations at temperatures in the range 250 – 290°C for ionic strengths ($I = (1/2) \Sigma C_i Z_i^2$) typical of our tests. In Eq. (4), Z_i is the ionic charge number and the limiting Debye-Hückel slope, S, is calculated as a function of temperature using the correlation developed by Sweeton et al.[11]

Combining Eqs. (2) - (4) yields

$$\log K_{eq} = \log Q + 12S\sqrt{I}/(1 + 1.75 \sqrt{I}) \qquad (5)$$

where $\qquad \log Q = -\log [Na^+]^4 [HPO_4^{2-}]^2 \qquad (6)$

An ion electroneutrality balance, which accounts for changes in water and phosphate ion dissociation behavior with temperature and ionic strength[11]-[13] was then employed to determine [H^+], hence [HPO_4^{2-}] at the Table I threshold conditions, cf. Ref. [2]. Table III summarizes all

9

calculated parameters needed to determine K_{eq} for Eq. (2). Figure 3 provides a plot of the resulting $\Delta G(T)$.

A constrained thermodynamic fit may be performed to determine $\Delta G°(298)$, $\Delta S°(298)$ and $\Delta C_p°(298)$ for Eq. (2). The analysis begins by invoking the isocoulombic principle.[14] This principle, which is applicable for describing ionic chemical reaction equilibria in aqueous media, states that $\Delta C_p°$ for the reaction will be zero if the reaction is written in a form that balances like charges on both sides of the equation. That is, by invoking phosphoric acid and water ionization equilibria, Eq. (2) may be rewritten in isocoulombic form as:

$$CrOOH(s) + 4Na^+ + 2H_3PO_4(aq) = Na_4Cr(OH)(PO_4)_2(s) + 4H^+ + H_2O \qquad (7)$$

Applying the results of Mesmer and coworkers, who obtained $\Delta C_p°$ for the phosphoric acid[12] and water[11] ionization reactions, it is estimated that $\Delta C_p° = 920$ J/(mol-K) for Eq. (2). This constraint allows K_{eq} for Eq. (2) to be least-squares fitted to the model

$$\Delta G(T), \text{ J/mol} = A - BT - 920T\ln T$$

Using the $\Delta G(T)$ data of Table III, it is found that $A = 41915$ and $B = -5595.2$ will provide free energy changes for Eq. (2) with a standard deviation of ± 5.2 kJ/mol over the temperature range $520 - 570$ K. The corresponding thermodynamic changes $\Delta G°(298)$ and $\Delta H°(298)$ for Eq. (2) are 147.3 and 316.2 kJ/mol, respectively. Table IV summarizes alkaline sodium phosphate-chromium(III) oxide system thermodynamics based on current literature.

ACKNOWLEDGEMENT

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TABLE I

Chromium Oxide Hydroxide Phase Transformation
Thresholds Observed in Sodium Phosphate Solutions

Test No.	Baseline Phosphate Molality	Na/P	Threshold Temp. °C	Final Phosphate Molality	Na/P	Indicated Na/P Loss
1	0.7407	2.332	256	0.7292	2.340	1.8
2	0.3627	2.333	260	0.3180	2.376	2.0
2A	0.3980	2.430	271	0.3806	2.450	2.0
3	0.1558	2.312	282	0.1495	2.324	2.0
4	0.7465	2.177	260	0.6786	2.192	2.0
5	0.3859	2.193	266	0.3327	2.246	1.9
6	0.1590	2.207	290	0.0974	2.332	2.0
7	0.7518	2.000	250*	0.7092	1.999	2.0
8	0.3648	1.996	257*	0.3243	1.997	2.0
9	0.1664	1.995	286*	0.1474	1.990	2.0

* The final temperatures for Tests 7 – 9 are 262, 276 and 297°C, respectively

TABLE II

Indexed Powder X-Ray Diffraction Pattern
Of Chromium(III) Oxide Hydroxide Reaction Product

Measured d spacing, Å	Pattern rel intens. I/I_o	Calcd d Spacing, Å	Refl. Plane Ind.			SIHP Pattern[3]	
			h	k	l	d(Å)	I/I_o
7.763	22	7.725	0	2	0	7.71	15
7.310	11	7.262	2	0	0	7.31	35
5.319	14	5.291	2	2	0	5.31	25
4.846	55	4.841	2	1	1	4.84	25
3.630	60	3.631	4	0	0	3.63	5
3.423	10	3.410	2	4	0	3.42	5
3.299	10	3.310	1	4	1	3.31	15
3.240	16	3.247	0	2	2	-	-
3.206	15	3.210	2	0	2	3.20	5
2.957	5	2.964	2	2	2	-	-
2.650	100	2.646	4	4	0	2.663	100
2.623	75	2.625	0	4	2	2.618	30
2.547	67	2.549	4	0	2	2.552	23
		2.542	5	2	1		
-	-					2.513	5
-	-					2.443	5
2.305	7	2.310	6	2	0	-	-
2.233	6	2.232	5	1	2	-	-
2.127	16	2.127	4	4	2	-	-
2.104	4	2.101	4	6	0	2.112	10
2.065	7	2.066	5	3	2	2.075	5
1.973	8	1.977	4	1	3	-	-
1.934	26	1.931	0	8	0	1.938	20
		1.930	7	2	1		
-						1.872	5
1.821	9	1.822	5	5	2	1.835	20
1.813	8	1.816	8	0	0	1.788	5
1.781	19	1.783	7	1	2	1.778	10
		1.780	6	4	2		
-	-					1.696	5
1.580	7	1.582	6	6	2	1.599	5
1.538	29	1.540	9	3	0	1.545	10
1.494	18	1.493	8	4	2	1.505	35
		1.489	6	5	3		
1.478	14	1.484	8	6	0	1.480	40
		1.478	5	9	0		
1.309	6	1.309	8	5	3	1.310	25

TABLE III

Solution Chemistry Values Used to Describe the CrOOH-$Na_4Cr(OH)(PO_4)_2$ Phase Boundary

Run No.	[Na^+] m	[HPO_4^{2}] m	I	S	Log Q	$\dfrac{12S\sqrt{I}}{1+1.75\sqrt{I}}$	ΔG^o kJ/mol
1	1.7274	0.7322	2.483	1.015	-0.6788	5.108	-44.83
2	0.8463	0.3607	1.211	1.037	1.1756	4.681	-59.77
2A	0.9685	0.3963	1.369	1.097	0.8596	5.054	-61.62
3	0.3603	0.1541	0.5147	1.166	3.3977	4.451	-83.44
4	1.6252	0.7414	2.378	1.037	-0.5837	5.188	-47.00
5	0.8463	0.3838	1.232	1.069	1.1217	4.839	-61.54
6	0.3509	0.1562	0.5073	1.224	3.4319	4.657	-87.29
7	1.5036	0.7391	2.244	0.9890	-0.4459	4.909	-44.70
8	0.7286	0.3548	1.084	1.023	1.4501	4.529	-60.71
9	0.3319	0.1563	0.4883	1.192	3.5281	4.497	-85.92

TABLE IV

Thermochemical Properties for Selected Species in the
Cr_2O_3-Na_2O-P_2O_5-H_2O System at 298.15K[a]

Species	$C_p^{\circ}(298)$	$S^{\circ}(298)$	$\Delta H_f^{\circ}(298)$	$\Delta G_f^{\circ}(298)$	Ref.
$Cr(OH)_3 \cdot 3H_2O(s)$	-	328.0	-1880.54	-1612.46	2
γ-$CrO(OH)(s)$	98.6	130.7	-710.64	-661.90	2
α-$CrOOH(s)$	-	110.8	-722.10	-667.40	15, 2
$Cr_2O_3(s)$	118.7	81.15	-1139.70	-1058.07	16, 17
$H_2O(aq)$	75.3	69.95	-285.83	-237.14	17
$H^+(aq)$	-71	-22.2	0	0	18, 16
$H_2PO_4^-(aq)$	37	72.4	-1308.8	-1130.8	18, 12
$HPO_4^{2-}(aq)$	-112	-32.6	-1305.5	-1089.7	18, 13
$PO_4^{3-}(aq)$	-283	-153.6	-1277.4	-1018.8	18, 16
$Cr^{3+}(aq)$	-	-367.8	-253.97	-215.48	19, 20
$Cr(OH)^{2+}(aq)$	-	-208.2	-497.96	-430.96	21
$Cr(OH)_2^+(aq)$	-	-140.6	-751.15	-628.15	21
$Cr(OH)_3(aq)$	-	-18.3	-1007.09	-844.40	2
$Cr(OH)_4^-(aq)$	-	89.3	-1214.54	-1007.75	2
$Cr(OH)_3(H_2PO_4)^-$	-	63.2	-2350.79	-2012.76	2
$Cr(OH)_3(HPO_4)^{2-}$	-	-74.0	-2340.99	-1955.43	2
$Cr(OH)_3(PO_4)^{3-}$	-	-100.9	-2284.47	-1884.25	2
$Cr(OH)_4(HPO_4)(H_2PO_4)^{4-}$	-	-115.0	-3935.07	-3261.47	2
$Na_4Cr(OH)(PO_4)_2(s)$	622	690.3	-3691.54	-3509.97	b

[a]Units: $C_p^{\circ}(298)$ and $S^{\circ}(298)$, J mol^{-1}K^{-1}; $\Delta H_f^{\circ}(298)$ and $\Delta G_f^{\circ}(298)$, kJ mol^{-1}. [b]This work.
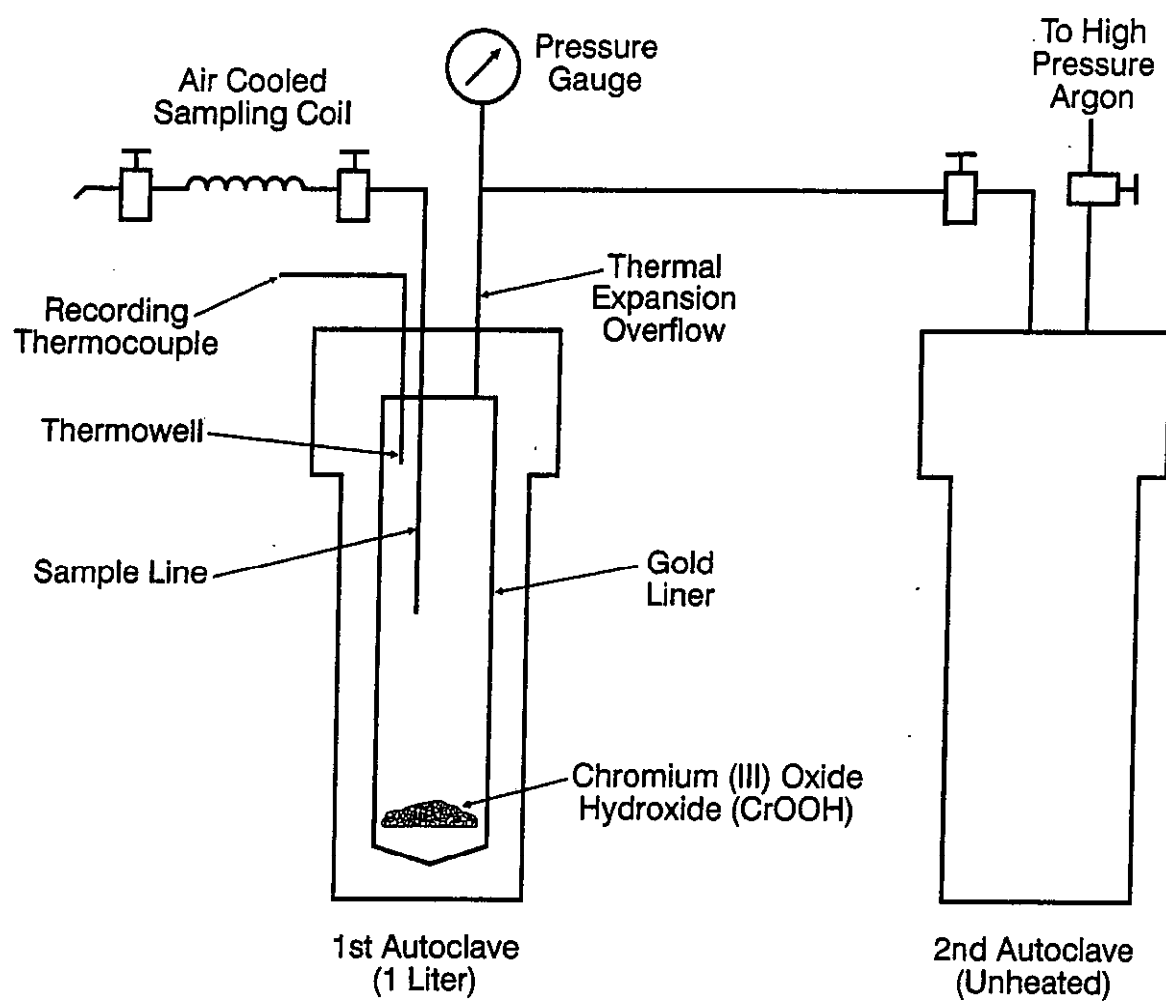
Fig. 1.   Schematic of autoclave arrangement used in
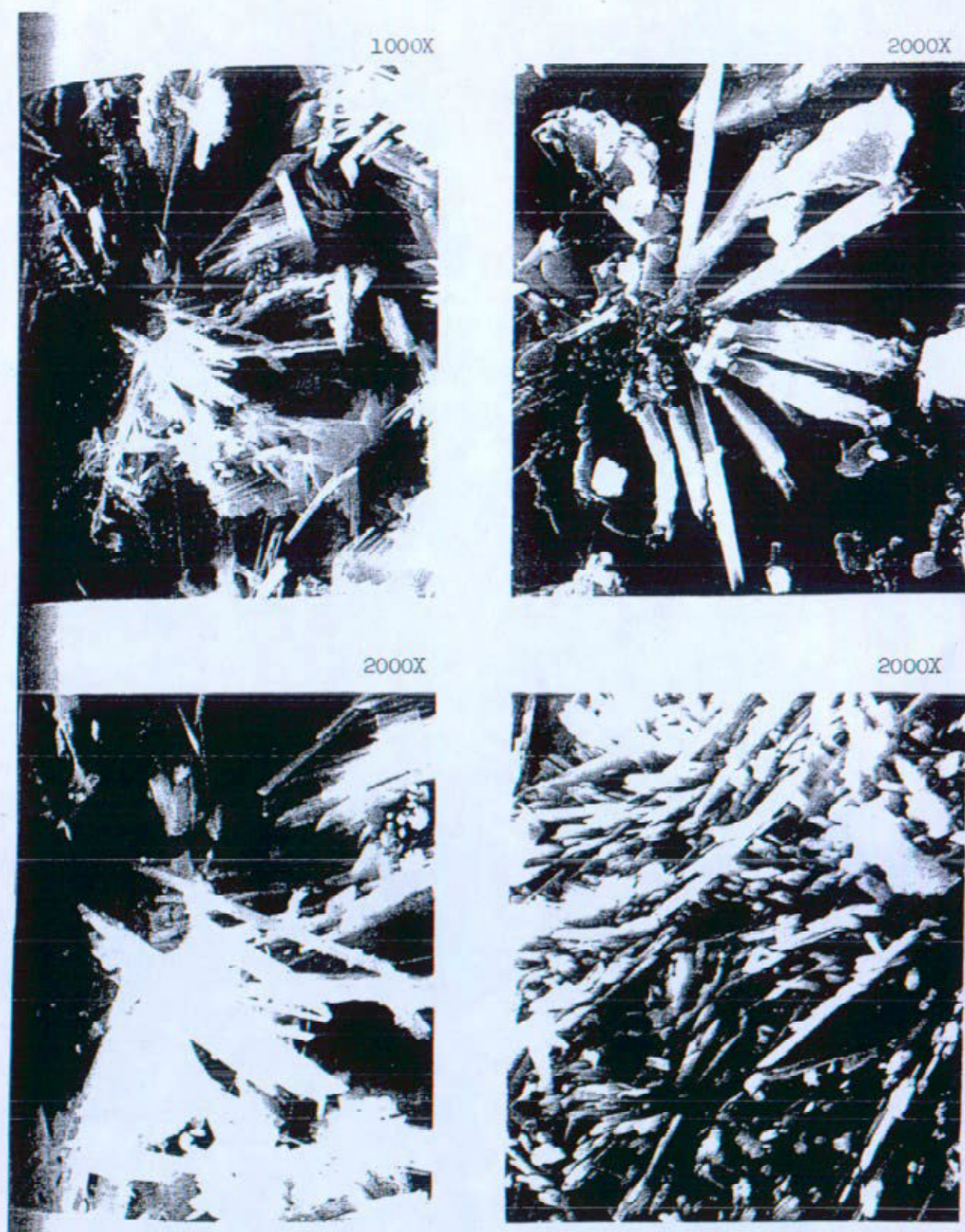   CrOOH transformation study

Fig. 2. Scanning electron microscope photographs of chromium(III) oxide hydroxide-sodium phosphate reaction products
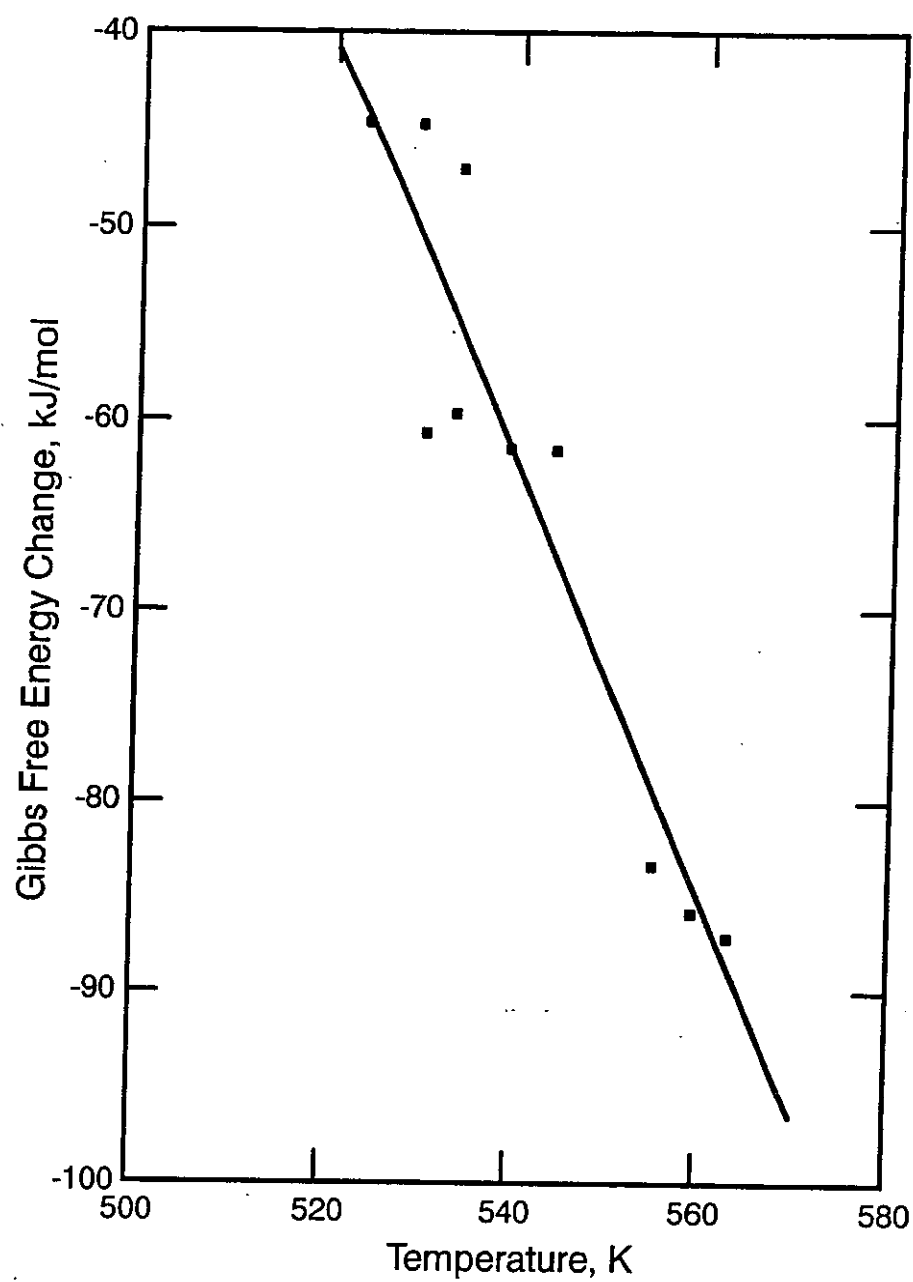
Fig. 3   Free energy changes determined for CrOOH transformation to sodium chromic hydroxyphosphate in alkaline sodium phosphate solutions.