HYDROTHERMAL SYNTHESIS OF ZINC SILICATES FROM BOROSILICATE GLASSES AND FROM MIXTURES OF ZINC OXIDE AND SILICA[†]

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Abstract—The formation of sauconite and hemimorphite from glasses and oxide precursors in aqueous solution at 150–200°C is described. A tentative schematic stability diagram for a portion of the system Na₂O–ZnO–SiO₂–H₂O at 150°C is presented. The relevance of this work to the use of a sodium zinc borosilicate glass as a matrix for the immobilization of nuclear fuel reprocessing wastes is discussed briefly.

The system $ZnO-SiO_2-H_2O$ includes two wellcharacterized zinc silicates: willemite, Zn_2SiO_4 and hemimorphite, $Zn_4Si_2O_7(OH)_2 \cdot H_2O$ (empirically, $Zn_2SiO_4 \cdot H_2O$). The univariant pressuretemperature curve for equilibrium (1) at pressures from 70 MPa to 10 GPa has been determined by Roy and Mumpton,¹ and by Pistorius.² Several zinc-containing phyllosilicates have

$$Zn_4Si_2O_7(OH)_2 \cdot H_2O \rightleftharpoons 2Zn_2SiO_4 + 2H_2O \quad (1)$$

been reported, both in nature³⁻⁶ and in preparative studies;⁷⁻⁹ little is known about their stability. Roy and Mumpton¹ concluded that a zinc end-member sauconite, namely $Zn_{x+y}[Zn_{3-x}(Si_{4-y}Zn_y)O_{10}(OH)_2]$ can occur stably below about 210°C at pressure near 100 MPa, and indicated that its stability is enhanced by partial substitution of Al for Zn. An Al-free natural sauconite was formulated by Smol'yaninova *et al.* as $Zn_3Si_4O_{10}(OH)_2 \cdot nH_2O$, and named zincsilite (see Ref. 4).

We have observed hemimorphite and a sauconite-like phase as products of hydrothermal devitrification of sodium zinc borosilicate glasses. This work formed part of an assessment of such glasses as host materials for nuclear fuel reprocessing wastes.¹⁰ In an attempt to clarify the occurrence of hemimorphite and sauconite, we

have also examined their formation from the parent oxides.

EXPERIMENTAL

Experiments were performed in 0.3 dm³-capacity titanium autoclaves using a heater and temperature control assembly described previously.¹¹ The preparation of sodium zinc borosilicate glasses has been described elsewhere;¹² experiments were run on both glass coupons and powders. The twelve glasses examined covered the composition range (mol per cent) 5-10 Na₂O, 5-30 ZnO, 10-40 B₂O₃, 40-70 SiO₂. Reagent grade powders of ZnO (surface area, estimated by BET method, $4 \text{ m}^2 \cdot \text{g}^{-1}$), quartz $(1 \text{ m}^2 \cdot \text{g}^{-1})$ and fused silica $(1 \text{ m}^2 \cdot \text{g}^{-1})$ were used. Crystalline products were isolated by filtration, air-dried and identified by X-ray powder diffractometry, using CuK_{α} radiation and a Philips PW-1150 diffractometer with a diffracted-beam monochromator.

RESULTS AND DISCUSSION

(a) Hydrothermal reactions of glasses

All the glasses examined underwent detectable surface crystallization during exposure to water for one day at 150°C. As expected, the quantity of crystalline products decreased, i.e. glass durability increased, with increasing silica content of the glass. These products were usually only loosely adherent on the surfaces of glass coupons. The solution pH, measured after cooling to room temperature, was usually 9–10.

The only observed crystalline products were hemimorphite and a sauconite-like clay. Most fea-

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tures in the diffraction pattern of the latter phase (see Table 1), were broad and ill-defined, which is typical of synthetic clays of this type.¹ The basal spacing of acetone-washed, air-dried material was near 12 Å, expanding to about 18 Å on saturation with glycerol or ethylene glycol. This clay was not chemically analyzed, since it was never obtained free of hemimorphite and/or amorphous material; we refer to it hereafter as sauconite.

In the reactions with glass coupons, sauconite occurred only on the most severely corroded glasses, which had low silica content; hemimorphite occurred on all other glasses. In the reactions with glass powders, sauconite was formed on most of the silica-rich glasses as well. Sauconite formation is thus favoured by a high ratio of glass surface area to solution volume, presumably due to more rapid glass dissolution. This suggests that sauconite occurred metastably in at least some experiments.

Sauconite persisted as the major solid product for up to 33 days at 200°C in some runs. However, when the solution was then replaced daily with distilled water, sauconite was converted to hemimorphite within three days. This shows that sauconite is not a congruently saturating phase (see Ref. 12), but it still could be stable at high silica and/or alkali activities.

(b) Hydrothermal reactions between ZnO and SiO_2

These experiments were intended to clarify the occurrence of sauconite; results are summarized in Table 2.

(i) Occurrence of willemite. Willemite was the sole product of reaction of a 2:1 mole ratio of ZnO and quartz in water at 225° C for 1 week. A similar reaction at 175° C yielded hemimorphite, with traces of willemite and residual starting materials. These results indicate that the equilibrium water partial pressure curve for reaction (1) intersects the water vapor pressure curve near 200°C, which is consistent with reported data at higher pressures.^{1,2}

(ii) Occurrence of hemimorphite. This phase occurred in 29 of 30 experimental runs with ZnO and quartz or fused silica in aqueous solutions at 150° C. It was the only zinc silicate formed in all runs with quartz, and in reactions between ZnO, fused SiO₂ and distilled water. It was also formed in about 20

hkl	Synthetic Sauconite ^a		Natural Sauconite ⁶		Montmorillonite	
	d,Å	Ie	d,Å	Ie	d,Å	I ^e
001	18.0	vs	16.6	100	17.6	100
002	9.0	s	8.33	100	9.00	50
003	6.1	vw?	(5.41?)	50b ^j	5.99	10
110 etc.	4.6	m,vb ^f	4.60	100	4.49	80
005	3.62	m	3.34	75	3.58	40
006	3.0	w,b?			2.99	30
130 etc.	26		2.62	764	2.57	40b
220 etc.	2.0	m,vo [,]	2.473	/30	2.242	10
009			—		1.989	5
240 etc.	1.7	w,vb	1.753	10	1.699	20
060 etc.	1.526	m	1.550	100	1.504	60

Table 1. X-ray diffraction data for synthetic sauconite and related solids

a Glycerol saturated, this work.

b Ethylene glycol saturated, JCPDS file card No. 8-444.

c Glycerol saturated sodium montmorillonite, JCPDS file card No. 12–219.

e b = broad, d = diffuse, m = medium, s = strong, v = very, w = weak.

f Peak at 4.6 Å with very broad asymmetric tail toward lower d.

g Obscured by hemimorphite peaks.

i Peak at 2.6 Å with very broad asymmetric tail toward lower *d*.

j Obscured by "Duco" band.

per cent yield from ZnO and quartz at 100°C for 1 week. In some reactions between ZnO and fused silica in alkaline solutions it occurred in association with sauconite.

(iii) Occurrence of sauconite. This phase was formed in several reactions between ZnO and fused silica in alkaline solutions $(0.01 \text{ mol} \cdot \text{dm}^{-3})$

 $Na_2B_4O_7$ or NaOH; 0.1 mol dm⁻³ NaOH) at 150°C. It did not occur in corresponding reactions with quartz replacing fused silica. It usually occurred in association with hemimorphite, but was the sole zinc silicate formed in one reaction between 1.0 g of ZnO and 2.4 g of fused silica in 150 cm³ of 0.1 mol dm⁻³ NaOH, unstirred, at

(A) Reactions using quartz								
ZnO:SiO ₂ mole ratio	Solution (M = mol \cdot dm ⁻³)	Temperature (°C)	Time (d)	Crystalline Products ^b				
2.0	H ₂ O	225	7	W				
2.0	H ₂ O	175	7	H (major)				
				Q,Z,W (minor)				
0.75	H ₂ O	175	7	H,Q (major)				
			_	Z (minor)				
0.75	H ₂ O	150	7	H,Q (major)				
			_	Z (minor)				
0.75	H ₂ O	100	7	Z,Q (major)				
				H (minor)				
0.62	0.01 M NaOH	137	4	H,Q (major)				
				Z (trace)				

Table 2. Products of reactions among ZnO, SiO₂ and various aqueous solutions^a

	(D) Meach	iono uonig juo	cu bio ₂	
0.62	H ₂ O	150	4	H (major)
				Z (trace)
0.62	H ₂ O	150	4	Н
0.30	H ₂ O	150	1	Z,H (major)
			7	Н
			28	Н
0.62	0.001 M NaOH	150	4	н
0.62	0.01 M NaOH	150	4	H (major)
				S (minor)
0.62	0.01 M NaOH	150	5,14	S (major)
				H (minor)
0.62 ^c	0.01 M NaOH	150	5	S (major)
				H (minor)
0.62 ^d	0.01 M NaOH	150	4	H
0.62	0.1 M NaOH	150	5	H (major)
				S (minor)
0.30	0.1 M NaOH	150	1	S (major)
				Z (minor)
			7,21	SÌ
0.62	0.01 M LiOH	150	4	S (major)
				H (minor)
0.62 ^e	0.01 M Na ₂ B ₄ O ₇	150	4	S (major)
				H (minor)
0.62	0.005 M Na ₂ SO ₄	150	4	Z

(B) Reactions using fused SiO₂

a Unless otherwise stated, reactions used 1.0 g ZnO and 175 cm³ of unstirred solution

b H = hemimorphite, Q = quartz, S = sauconite, W = willemite, Z = ZnO

c 4.0 g ZnO, 4.8 g SiO₂, 700 cm³ solution, stirred

d 0.5 g ZnO, 0.6 g SiO₂, 700 cm³ solution, stirred

e Duplicated run.

150°C for seven days. Analysis of this material, which was contaminated with unreacted ZnO and SiO₂, indicated a sodium content of about 1 wt.%, compared with 1.5% expected for the ideal montmorillonoid composition $Na_{0.333}Zn_{2.833}Si_4O_{10}$ (OH)₂. We conclude that sodium is probably an essential constituent of the sauconite prepared in these reactions.

(iv) Interconversion of sauconite and hemimorphite. Several experiments were run to try to determine the conditions of equilibrium (2) at 150° C. represents the solubility of willemite (W). Lines H and W will approach one another with increasing temperature, and cross over at the hemimorphite + willemite + solution + vapour quadruple point near 200°C. The solubility of sauconite (S) is a line of approximate slope -1.4, the precise value depending on the exact stoichiometry.

Sauconite was formed from ZnO and fused silica in 0.01 mol \cdot dm⁻³ NaOH, so line S lies to the left of point *a* (Fig. 1) under these conditions. Since sauconite is not a stable saturating phase in 0.1 mol \cdot dm⁻³ NaOH, line S must lie to the right

$$17Zn_{4}Si_{2}O_{7}(OH)_{2} \cdot H_{2}O + 8Na^{+} + 8OH^{-} + 62SiO_{2} \rightleftharpoons 24Na_{0.333}Zn_{2.833}Si_{4}O_{10}(OH)_{2} + 14H_{2}O$$
(2)
hemimorphite sauconite

In the presence of fused silica at 150°C, hemimorphite persisted unchanged for 28 days in water, and for 7 days in 0.1 mol \cdot dm⁻³ NaOH. Sauconite also persisted in the presence of fused silica in 0.1 mol · dm⁻³ NaOH for 21 days. Under somewhat more aggressive conditions— $0.5 \text{ mol} \cdot \text{dm}^{-3}$ NaOH at 175°C-both sauconite and hemimorphite reacted in the presence of fused silica to produce quartz and at least one unidentified phase. The latter did not correspond to any of the numerous sodium zinc silicates reported in Refs. 14-17. Kinetic limitations would thus not permit direct determination of the conditions of equilibrium (2). However, when a mixture of sauconite and hemimorphite (0.5 g total) was allowed to react with $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ NaOH} (700 \text{ cm}^3) \text{ at } 150^{\circ}\text{C}$ for seven days, the solid product was pure hemimorphite. This supports our earlier deduction that sauconite is not a congruently saturating phase.

(c) Deduction of stability relationships

Although equilibrium relationships could not be determined, we can deduce certain limitations on the stability of sauconite, as shown in Fig. 1. This figure shows schematically the solubilities of the various solids, expressed as activities of aqueous $Si(OH)_4^{\circ}$ and $Zn(OH)_2^{\circ}$. Since the formation of ZnO, SiO_2 and hemimorphite from these two species does not involve net reaction of protons, these solubility lines are pH-independent. (The solubilities expressed as total Zn and/or Si concentrations are pH-dependent.) However, sauconite formation probably involves NaOH (e.g. reaction (2)), so the sauconite solubility line will move to the left with increasing Na⁺ and OH⁻ activities.

The horizontal and two vertical lines in Fig. 1 represent the solubilities of ZnO (Z), quartz (Q) and fused silica (F), respectively. The solubility limit of hemimorphite (H) is a line of slope -0.5. A parallel line at slightly higher solute activities

of point b. Our inability to produce sauconite from ZnO and quartz, even in alkaline solution, implies that conditions for sauconite nucleation are hard to achieve to the left of line Q, but does not impose definite limits on sauconite stability.

CONCLUSIONS

Hemimorphite appears to be the only stable solid zinc silicate in the system $ZnO-SiO_2-H_2O$ at 150°C. Sauconite is stable with respect to ZnO and fused silica in 0.01 mol \cdot dm⁻³ NaOH at 150°C, but is probably metastable with respect to hemimorphite and quartz, even in NaOH solution. However, sauconite can be persistent, and its conversion to hemimorphite, even at 200°C, can be very slow.

The reaction of stoichiometric quantities of ZnO and SiO₂ in water provides convenient small-scale synthetic routes to hemimorphite (at 150–175°C) and willemite (at 225°C). It is very difficult to



Fig. 1. Schematic representation of solubility relationships among solids in the system $ZnO-SiO_2-H_2O$ at 150°C, expressed as activities of $Zn(OH)_2^{\circ}(aq)$ and $Si(OH)_4^{\circ}(aq)$. F = fused SiO₂, H = hemimorphite, Q = quartz, S = Na-containing sauconite, S' = Na-free sauconite, W = willemite, Z = zinc oxide. The hatched lines indicate equilibrium saturating solids.

prepare pure sauconite from ZnO and fused silica, but the best conditions are near 150°C, unstirred, in 0.1 mol \cdot dm⁻³ NaOH.

We reach the following tentative conclusions about hydrothermal alteration of a high-level radioactive waste product comprising a dilute solution of radionuclides in a zinc-containing sodium borosilicate glass:

(i) Crystallization of hydrated zinc silicates is likely to occur readily on exposure to water at 150–200°C, and probably also at lower temperatures.

(ii) Since these products are only loosely adherent on corroding glass surfaces, they are unlikely to aid passivation of the glass. Indeed, they could promote corrosion by providing a sink for dissolved Zn and Si close to the corroding surface.

(iii) The formation of sauconite is probably preferable to that of hemimorphite, since a montmorillonoid product is likely to have more desirable ion-exchange and solid-solution properties for the retention of some radionuclides. However, being metastable, sauconite is unlikely to persist indefinitely. In general, it may be possible to tailor radioactive waste glass compositions to promote their alteration to stable clay products, perhaps by addition of Al_2O_3 .

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