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Phase equilibrium study in the $CaO–K_2O–B_2O_3–H_2O$ system at 25°C

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Abstract

The $CaO-K_2O-B_2O_3-H_2O$ system has been investigated at 25°C by extending experimentally data in the literature. By analogy with the corresponding known Na-borates, seven supersaturated mixtures of similar alkali/boron molar ratios were prepared but with potassium substituting for sodium. The mixtures were shaken regularly and attainment of the equilibrium state was monitored by flame emission spectroscopy for potassium. Equilibria were established typically after 1–3 months. The solids in the mixtures were identified by X-ray diffraction technique, and the solutions were analysed using ICP-spectroscopy. Solubility data of $KB_5O_8{\cdot}4H_2O$, $KB_3O_3(OH)_4{\cdot}2H_2O$, $K_2B_4O_5(OH)_4{\cdot}2H_2O$, $KBO_2{\cdot}1.25H_2O$, and $K_2CaB_8O_{14}{\cdot}12H_2O$ were determined and used to extend the database of the thermodynamic modelling computer code PHREEQC. Phase diagrams of the $CaO-K_2O-B_2O_3-H_2O$ system and its subsystems were constructed for 25°C.

Keywords: Thermodynamic calculations; CaO; KOH; Borate; Modelling

1. Introduction

Borates applied as moderator material in PWRs cannot be reused after a certain operation period and must be disposed of. Classified as medium level radioactive waste, solidification in cement paste seems to be a suitable option, although the strong set retarding effect of borates need to be overcome by addition of significant amounts of alkali hydroxide. For example, sodium hydroxide added at a Na/B molar ratio of about 2.5 or more restores setting times to normal [1]. Phase relations and optimum quantity of sodium, including thermodynamic modelling in the system $Na_2O-B_2O_3-CaO-H_2O$, have been published [2].

The present work investigates the behaviour of another common alkali metal, potassium, in order to facilitate practical work for immobilisation of waste boron effluents by determining the optimum quantity of potassium to be added to achieve proper confinement. Typical constituents of cementitious systems are aqueous calcium and alkali compounds and their various combinations. The computer code used (PHREEQC [3]) calculates solubility indices that indicate the supersaturated solid phases that are most likely to precipitate in a given assemblage. Additionally, the program output contains data on composition of the liquid in equilibrium of the above phase(s) as well as aqueous pH values, etc. This enables plotting of phase diagrams solely by calculation, although it strictly requires that all possibly encountered phases be considered otherwise the calculation results in large errors. The most important consti-

Table 1
Initial composition of supersaturated sample mixtures

		Admixed quantities			
Sample	Target ratios[a]	$Ca(OH)_2$, g	KOH, g	H_3BO_3, g	H_2O, ml
1	0:1:5:10	–	6.131	33.780	100
2	0:1:2:10	–	20.454	46.177	100
3	0:1:1:8	–	53.914	59.405	40
4	0:2:1:X	–	66.030	36.620	50
5	2:1:5:16	1.013	0.767	4.221	100
6	2:2:5:15	0.808	1.223	3.369	100
7	1:8:16:160	7.404	44.888	98.928	900

[a] Target ratios indicate components in the order $CaO-K_2O-B_2O_3-H_2O$.

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Table 2
Aqueous and solid phase compositions in equilibrium

Sample	K, mol/l	B, mol/l	Ca, mol/l	Observed solids
1	0.0796	1.1800	–	$KB_5O_8 \cdot 4H_2O$
2	2.2840	3.2200	–	$KB_5O_8 \cdot 4H_2O$, $K_2B_4O_5(OH)_4 \cdot 2H_2O$
3	1.8540	1.8500	–	$K_2B_4O_5(OH)_4 \cdot 2H_2O$, $K_4H_2(CO_3)_3 \cdot 1.5H_2O$
4	4.0440	2.5900	–	$K_2B_4O_5(OH)_4 \cdot 2H_2O$, $KBO_2 \cdot 1.25H_2O$, $K_2CO_3 \cdot 1.5H_2O$ (traces)
5	0.0611	0.3478	0.00609	$Ca(OH)_2$
6	0.2159	0.2850	0.00377	$CaB_2O_4 \cdot 4H_2O$, $Ca(OH)_2$
7	0.7352	0.6477	0.00036	$K_2CaB_8O_{14} \cdot 12H_2O$, $CaB_2O_4 \cdot 4H_2O$, $Ca_2B_6O_{11} \cdot 13H_2O$

tuents of the database are the solubility products and dissociation equations of the given compounds. Lacking those data from reliable literature sources, experimental work has had to be carried out to obtain precise and validated values.

2. Experimental

By analogy with the previously studied system with sodium [2], seven different deliberately supersaturated solutions were prepared at various potassium/boron ratios corresponding to the relevant sodium borates (Table 1). Mixes were kept at 25°C and shaken frequently to hasten dissolution/precipitation processes; elevated temperatures were not used. Achievement of an equilibrium state is most conveniently checked by monitoring the aqueous concentration of a readily determined component, e.g., potassium, therefore, FES measurements have been performed on a regular basis. It was observed that potassium concentrations needed about 4 weeks to become unchanged, which was indicated by similar values measured in comparison to readings at an age of 3 weeks. Following this equilibrium state, albeit assumed, the mixes were filtered and dried in air. A qualitative analysis of the solids formed was performed and chemistry of the mother liquor measured, in addition to determination of the relevant solubility products. These were done by X-ray diffraction and spectroscopic techniques (flame emission for K, ICP-S for Ca and B), respectively. Equilibrium compositions observed are included in Table 2.

2.1. Inclusion of new data to the database of the computer code PHREEQC

The first task extending the database is to revise speciation of the code in respect to the elements of the system studied. In the case of boron, for example, it means inclusion of polymeric borate species [4,5]. The next step is to construct the solid phase(s) using the species available in the code, i.e., to write appropriate solubility equations with the help of standard dissociation elements (Table 3). Relevant species in the database are as follows: Ca^{+2} K^{+}, H_3BO_3, H^{+}, and H_2O. Although not observed in this series of mixtures, the compound $KB_3O_3(OH)_4 \cdot 2H_2O$ was still included in the database for completeness as it may precipitate if conditions change. It was actually observed in small quantities together with $K_2B_4O_5(OH)_4 \cdot 2H_2O$ and $KBO_2 \cdot 1.25H_2O$, probably as a metastable phase, when the filtered mother liquor of Sample 6 was allowed to evaporate.

At the start, the sample in which only one compound has been precipitated was selected. For this compound its $\log K_{sp}$ value can be calculated with the help of the relevant aqueous phase concentration by following the procedure below: first the compound is constructed using the species required by the program. Then a dummy value for the compound is entered in the database for its $\log K_{sp}$ value, which of course is not the proper one. In running the program to calculate solid phase(s) precipitating from a given concentration solution, one is required to enter composition of the equilibrium solution and, as a result, solubility index (SI) for the appropriate compound is obtained. This SI value is actually the

Table 3
Compounds, their designation and dissociation species entered in the database as well as the calculated $\log K_{sp}$ values

Compound and designation	Ca^{+2} [number]	K^{+} [number]	H_3BO_3 [number]	H^{+} [number]	H_2O [number]	$\log K_{sp}$ value
$KB_5O_8 \cdot 4H_2O$ (santite), 1.5.8K	0	1	5	− 3	− 1	3.19
$K_2B_4O_5(OH)_4 \cdot 2H_2O$, 1.2.4K	0	2	4	− 1	− 2	12.86
$KBO_2 \cdot 1.25H_2O$, 2.2.5K	0	1	1	− 1	0.25	9.50
$KB_3O_3(OH)_4 \cdot 2H_2O$, 1.3.8K	0	1	3	− 1	0	5.50
$K_2CaB_8O_{14} \cdot 12H_2O$, Ca·1.4.12K	1	2	8	− 4	2	15.62

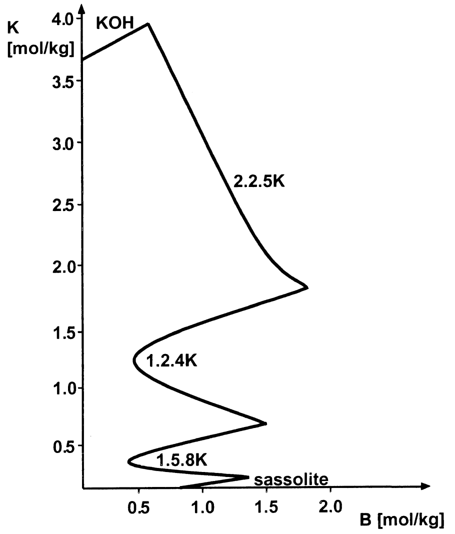

Fig. 1. Phase equilibrium diagram of the system $K_2O-B_2O_3-H_2O$ at 25°C.

difference of the logarithm of the actually observed ion activity product (logIAP) and the logarithm of the solubility product ($\log K_{sp}$); for the latter we may have given an inappropriate value. The value of SI indicates behaviour of the system: a positive value means that the given compound is supersaturated and likely to precipitate, whereas a negative value means that species of the dissociated compound are undersaturated, its precipitation does not occur. An equilibrium state is indicated by SI being zero. This is the very case which was experimentally determined, so the logIAP value calculated by the program may also be taken as $\log K_{sp}$. Once calculated and entered into the database, another sample containing this compound, plus one with unknown $\log K_{sp}$, is selected and the above procedure repeated to obtain another $\log K_{sp}$ in the system.

When all mixes have been used to determine the real $\log K_{sp}$ values of the appropriate solids (Table 3), investigation and validation of multicomponent systems can commence using the now complete database. Compositions of invariant points and boundary curves can also be calculated. Incompatibility is signalled by supersaturation (SI > 1) of the aqueous phase for additional solid(s) than equilibrated. The performed phase equilibrium calculations resulted in plotting the phase diagram of the $K_2O-B_2O_3-H_2O$ system in Fig. 1, which has been found identical to that in the literature [6].

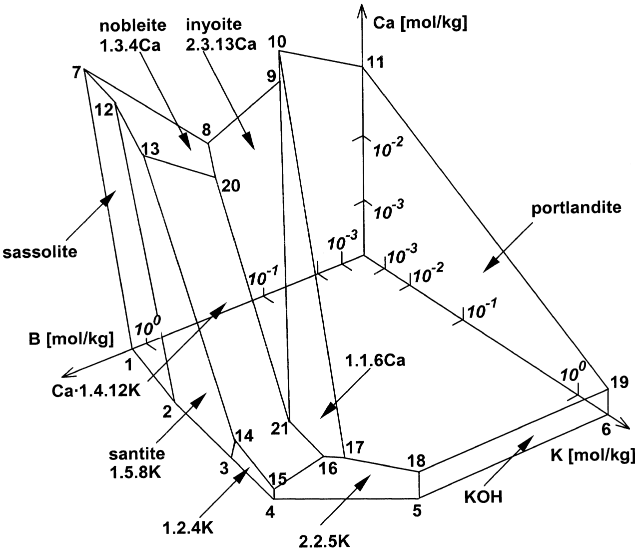

Fig. 2. Perspective demonstration of saturation surfaces in the system $K_2O-B_2O_3-CaO-H_2O$ at 25°C. Note axes are logarithmic and phase diagram is schematic for simplicity, primary fields are concave surfaces in reality. For notation of solids see Table 4. Numbers refer to the invariant points shown in Table 5.

With this as a starting point, calculations have been extended to the system with CaO in increasing amounts. Constituent solids are listed in Table 4, results of the calculations illustrated in Fig. 2, and compositions of the invariant points given in Table 5. Literature reports rapid formation of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ in chloride-contain-

Table 4
Nomenclature of solids in the system $K_2O-B_2O_3-CaO-H_2O$ at 25°C

Notation or chemical name	Mineral name	Formula
boric acid	sassolite	H_3BO_3
1.3.4Ca	nobleite	$CaO{\cdot}3B_2O_3{\cdot}4H_2O$ or $Ca[B_3O_3(OH)_4]_2$
2.3.13Ca	inyoite	$2CaO{\cdot}3B_2O_3{\cdot}13H_2O$ or $Ca_2[B_3O_3(OH)_5]_2{\cdot}8H_2O$
1.1.6Ca	hexahydroborite	$CaO{\cdot}B_2O_3{\cdot}6H_2O$ or $Ca[B(OH)_4]_2{\cdot}2H_2O$
calcium hydroxide	portlandite	$Ca(OH)_2$
Ca·1.4.12K	n/a	$K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ or $K_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O$
potassium hydroxide	n/a	KOH
2.2.5K	n/a	$2K_2O{\cdot}2B_2O_3{\cdot}5H_2O$ or $KBO_2{\cdot}1.25H_2O$
1.2.4K	n/a	$K_2O{\cdot}2B_2O_3{\cdot}4H_2O$ or $K_2B_4O_5(OH)_4{\cdot}2H_2O$
1.5.8K	santite	$K_2O{\cdot}5B_2O_3{\cdot}8H_2O$ or $KB_5O_6(OH)_4{\cdot}2H_2O$

Table 5
Calculated phase equilibrium results of the system $K_2O-B_2O_3-CaO-H_2O$ and its subsystems (position of the various points can be seen in Fig. 2)

				Equilibrium solution concentrations (mol/kg)			
Invariant point	Equilibrium solid phases			B	K	Ca	pH
1	Sassolite	–	–	1.008	–	–	2.794
2	Sassolite	1.5.8K	–	1.360	0.078	–	4.379
3	1.5.8K	1.2.4K	–	1.530	0.678	–	8.995
4	1.2.4K	2.2.5K	–	1.877	1.890	–	12.563
5	2.2.5K	KOH	–	0.5923	3.965	–	14.222
6	KOH	–	–	–	3.673	–	14.260
7	Sassolite	1.3.4Ca	–	1.729	–	8.081×10^{-2}	4.661
8	1.3.4Ca	2.3.13Ca	–	0.3035	–	1.610×10^{-2}	7.052
9	1.1.6Ca	2.3.13Ca	–	0.04696	–	2.640×10^{-2}	11.602
10	1.1.6Ca	Portlandite	–	0.04375	–	3.972×10^{-2}	12.350
11	Portlandite	–	–	–	–	2.041×10^{-2}	12.468
12	1.5.8K	Sassolite	1.3.4Ca	1.804	0.042	6.775×10^{-2}	4.699
13	Ca·1.4.12K	1.3.4Ca	1.5.8K	1.154	0.065	2.554×10^{-2}	5.471
14	1.2.4K	1.5.8K	Ca·1.4.12K	1.530	0.678	5.635×10^{-11}	8.995
15	1.2.4K	2.2.5K	Ca·1.4.12K	1.877	1.890	4.656×10^{-10}	12.563
16	Ca·1.4.12K	1.1.6Ca	2.2.5K	1.365	2.339	9.542×10^{-5}	13.688
17	Portlandite	1.1.6Ca	2.2.5K	1.117	2.709	1.636×10^{-4}	13.898
18	2.2.5K	Portlandite	KOH	0.5922	3.965	5.260×10^{-5}	14.222
19	Portlandite	KOH	–	–	3.673	5.215×10^{-5}	14.260
20	Ca·1.4.12K	1.3.4Ca	2.3.13Ca	0.3091	0.005	1.464×10^{-2}	7.073
21	Ca·1.4.12K	1.1.6Ca	2.3.13Ca	0.6442	0.734	3.635×10^{-4}	12.724

ing solutions [7], but this compound was observed in chloride-free solution after 3 weeks only.

3. Conclusions

It can be deduced from the phase equilibrium calculations that the shape and limits of stability fields (positions of invariant points) of potassium borates formed are little changed as a function of Ca concentration in their entire stability fields. Santite is the most stable compound in terms of increasing Ca concentration (~ 0.07 M), whereas other potassium-borate-hydrates typically transform to calcium-borate-hydrates and/or portlandite at about three orders of magnitude lower calcium levels.

Shapes of stability fields of calcium borates are hardly changed with increasing aqueous Ca concentration either; however, their boundary curves shift to lower B and K concentrations with the exception of nobleite ($CaO{\cdot}3B_2O_3{\cdot}4H_2O$). Based on the above reasons, as well as experimental observations, the following conclusions can be drawn concerning primary stability fields of potassium-borate-hydrates.

3.1. 1.2.4K

Potassium diborate precipitates only if the molar ratio of K_2O:B_2O_3 is between 0.1–1.4, and at the same time the concentration of boron exceeds 1 mol/kg, and that of potassium exceeds the 0.5 mol/kg value. Its field of stability is within the pH range of 9–11 (calculation predicts up to 12.5).

3.2. 2.2.5K

Potassium borate precipitates only when potassium is sufficiently concentrated, typically exceeding 1.8 mol/kg. The molar ratio of K_2O:B_2O_3 is between 1.6–2.0. Precipitation of this potassium borate is experienced if pH is between 11–12.5 (somewhat lower than predicted by calculation).

3.3. 1.3.8K

This potassium borate is not expected to form at 25°C due to its good solubility, yet its saturation index is just under zero. Other K-borate-hydrates (1.2.4K and 1.5.8K) would precipitate instead.

3.4. 1.5.8K

This compound precipitates at the smallest K concentrations (>0.08 mol/kg). The reasons for this are to be seen in its formula since the molar ratio of K_2O:B_2O_3 is about 0.2. To obtain this phase, the concentration of boron should exceed 1.5 mol/kg with pH between 5–9 (which agrees well with calculation).

3.5. Ca·1.4.12K

$K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ has a different alkali/calcium ratio than for ulexite ($Na_2O{\cdot}2CaO{\cdot}5B_2O_3{\cdot}16H_2O$). It precipitates from an aqueous solution of CaO:K_2O:B_2O_3 molar ratios of 1:4:8, which is far from the elemental ratios in the solid (1:1:4). At start the mixture is amorphous, crystals appear after stirring for 3 weeks. The actual pH value of the solution (pH = 10.2) is lower than the calculated one (pH = 12.7).

It is important from a waste immobilisation point of view how portlandite solubility is affected by K_2O, by B_2O_3, and by mixtures thereof. Portlandite solubility doubles on addition of B until the binary invariant point of portlandite–hexahydroborite is reached, whereas on addition of K it decreases by more than three orders of magnitude (see points 10 and 19 in Fig. 2, respectively). As a combined effect of K_2O and B_2O_3, the stability field of portlandite is extended to much higher borate concentrations (from 0.047 M at point 10 up to 1.117 M at point 17, Fig. 2), but with similarly decreasing Ca concentrations as for K_2O addition alone. Comparison with the corresponding system with sodium instead of potassium [2] shows that solubility-limiting phases establish aqueous borate concentrations at about twice as low as for their sodium counterparts.

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