STRUCTURE OF MD SIMULATED CALCIUM ALUMINOSILICATE SYSTEMS

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Molecular dynamics simulations of the $CaO-Al_2O_3-SiO_2$ system imply a different behaviour for the Si and Al atoms in the formation of aluminosilicate polyanions that is also influenced by their polymerization degree. Although both Si and Al in simulated systems prefer tetrahedral coordination by oxygen, the Al atoms are situated in the most branched positions so that they are bound mainly to bridging oxygen atoms while the Si atoms prefer bonding to non-bridging oxygen atoms. Increased polymerization is accompanied by the presence of 1 - 5 % of TO_5 groups (T = Si, Al). In the most polymerized system, about 7 % of the oxygen atoms were observed to be bound to three T atoms.

INTRODUCTION

The great importance of aluminosilicates in geological processes as well as in glass, ceramics and cement technology has stimulated extensive experimental studies aimed at understanding the relations between the structure and properties of these systems. Despite the great quantity of useful knowledge collected, some experimental data are difficult to interpret unambiguously.

Consequently, this is the place for theoretical methods, mainly modelling techniques that enable the investigation of various influential factors which affect the experimental data.

This work presents the results of molecular dynamics simulations for 4 calcium aluminosilicate systems with constant Al:Si ratio (Al / Si = 1) to investigate the effect of different polymerization degree on the distribution of the Si and Al atoms in the polyanions. The compositions of the systems are shown in table 1.

EXPERIMENTAL PART

The simulated ensembles each contained about 850 particles and Born-Mayer-Huggins pair potential functions (PPFs) were used to model the interionic interactions [1,2]. All the simulations started from a random ion distribution at 6000 K. The densities of the systems were adjusted at 6000, 2000, 1000 and 400 K to achieve "zero pressure" (less than 5 kPa). The systems were cooled in steps of 1000 K from the starting temperature down to 2000 K and then in steps of 100 K up to 400 K. They were kept at each temperature for 10000 simulation steps (10 ps); 2 ps of velocity scaling to reach the temperature and 8 ps of equilibration. The data collecting, so called measurement, took place during the last 1050 steps of the equilibration. The simulations were performed using a modified version of the P3M3DP program from the CPC Program Library [3].

All of the structural results presented are referred to the measurement at 400 K . The average coordination

Table 1. Compositions of the simulated systems, stoichiometric Q^n structural units (defined in the text), average coordination numbers for the network forming atoms, T, (T=Si, Al) and the numbers of bridging oxygen atoms (BO) bound to T.

			coord. number			BO/T		
system	str.unit	composition	T	Si	Al	T	Si	Al
CAS11	Q^1	$7CaO.Al_2O_3.2SiO_2$	4.00	4.00	4.00	1.49	0.72	2.25
CAS10	Q^2	$5CaO.Al_2O_3.2SiO_2$	4.01	4.03	4.00	2.14	1.52	2.76
CAS5	Q^3	$3CaO.Al_2O_3.2SiO_2$	4.02	4.02	4.02	3.05	2.52	3.57
CAS2	Q^4	$CaO.Al_2O_3.2SiO_2$	4.05	4.06	4.05	3.96	3.90	4.02

numbers were obtained by integration of the first peak in the radial distribution functions (RDFs) to the following minimum.

RESULTS

Polymerization degree

The compositions of the simulated systems were chosen so that the overall polymerization degree would increase stepwise from the stoichiometry with 1 bridging oxygen atom (BO) per TO_4 tetrahedron, also referred to as a Q^1 group for CAS11, to 4 BO per TO_4 for CAS2 - Q^4 group (table 1). The simulation results follow this change in the polymerization degree; nevertheless, the divergence from the idealized stoichiometry is most pronounced for CAS11 and decreases for the more polymerized systems. In the case of CAS2, not only the number of non-bridging oxygen atoms (NBO) is almost zero, but the presence of so called "triclusters" (OT_3) - oxygen atoms bound to 3 network forming atoms T (T=Si,Al) [4] - even increases the high crosslinking.

A great difference in the distribution of the BO and NBO (non-bridging oxygen) between Si and Al atoms is observed for all compositions. Si atoms are found at less polymerized sites in the aluminosilicate polyanions, unlike Al atoms which are at their most branched positions. This is in excellent agreement with Mysen's conclusions concerning the structure of peralkaline aluminosilicate melts and glasses, based on spectroscopic measurements [5].

Coordination of network forming atoms

The majority of the Si and Al atoms have tetrahedral coordination by oxygen atoms in all of the simulated systems. The average coordination numbers are shown in table 1. The SiO_4 terahedra are less distorted than the AlO_4 tetrahedra and the deviations from the ideal tetrahedral geometry increase slightly from the least polymerized CAS11 to CAS2. The average Si-O bond length ranges from 0.162 nm to 0.165 nm in the simulated systems, which is very close to the experimentally observed values [6,7]. The Al-O bonds are slightly longer, by about 0.01 nm, than the experimental values of 0.175-0.181 nm obtained from EXAFS data [6,8].

Together with tetrahedral coordination, 5-coordinated Si and Al atoms are observed in the more polymerized systems. The CAS2 system, whose composition corresponds to the idealized stoichiometry of a fully polymerized framework of SiO_4 and AlO_4 tetrahedra, contains the highest number of these structural units. In this system both 3- and 6-coordinated Al atoms are also observed. While the 3-coordinated sites seem to be permanent components, the 6-coordination is clearly a transition configuration only, because its relative abundance of 0.2 % of all of the Al atoms corresponds to less than 1 such configuration per simulation step. The AlO_3 groups have a planar geometry and they were also observed in other simulation results [9]. As all 3 oxygens of this group form bridges to another central atom, it can be considered as a neutral aluminium species resembling BO_3 triangles in B_2O_3 and borosilicates.

DISCUSSION

Second coordination sphere of network forming atoms

The constant ratio, Si / Al = 1, in the simulated systems is a good basis for studying the mutual ordering of the SiO_4 and AlO_4 tetrahedra as a function of polymerization degree. Fully polymerized crystalline materials with this Si/Al ratio are built up of regularly ordered SiO_4 and AlO_4 units interconnected through all their vertices into four and six membered rings. Only Si-O-Al bridges are present, which complies with the Loewenstein's aluminium avoidance principle. In the case of glasses and melts of the same composition, there are some controversial interpretations of both thermodynamic and spectral data [5]. Molecular orbital calculations [10] imply a higher stability of Si-O-Al linkages compared to Si-O-Si and Al-O-Al, although the MO estimates of the enthalpy for the reaction

$$(M^{n+})\ 1\ /\ n\mathrm{AlO_2} + \mathrm{SiO_2} \rightleftharpoons (M^{n+})1/n\mathrm{AlSiO_4} \qquad (1)$$

(n-valence of the charge balancing cation) is highly overestimated. As calorimetric data show, the reaction enthalpy depends on the type of charge balancing cation M^{n+} and becomes more exothermic with decreasing of M^{n+} field strength, z/r^2, in the sequence $Mg^{2+} > Ca^{2+} > Na^+ > K^+$. The values range roughly from 10 to 60 kJ mol^{-3} [10] and so they are not too high to prohibit quite considerable Si-Al disorder not only in melts and glasses, but also in the crystalline framework aluminosilicates at high temperatures. On the other hand, ^{29}Si and ^{27}Al magic angle spinning NMR spectroscopic measurements for $CaAl_2Si_2O_6$ glass, interpreted in the terms of $Q^4(nAl)$ species (SiO_4 groups with 4 BO with n of them bound to Al and the rest (4-n) to other Si atoms) indicate only the presence of $Q^4(4Al)$ [11]. For nepheline composition glass, a low intensity signal was also detected for $Q^4(3Al)$ [12]. Although the detection limit of 10 - 15 % for NMR measurements is taken into account, these results suggest rather high ordering of the Si and Al atoms in these systems.

The mutual ordering of the Si and Al atoms in the simulated systems changes substantially with the polymerization degree. Figure 1 shows RDFs for the Si-Si, Si-Al

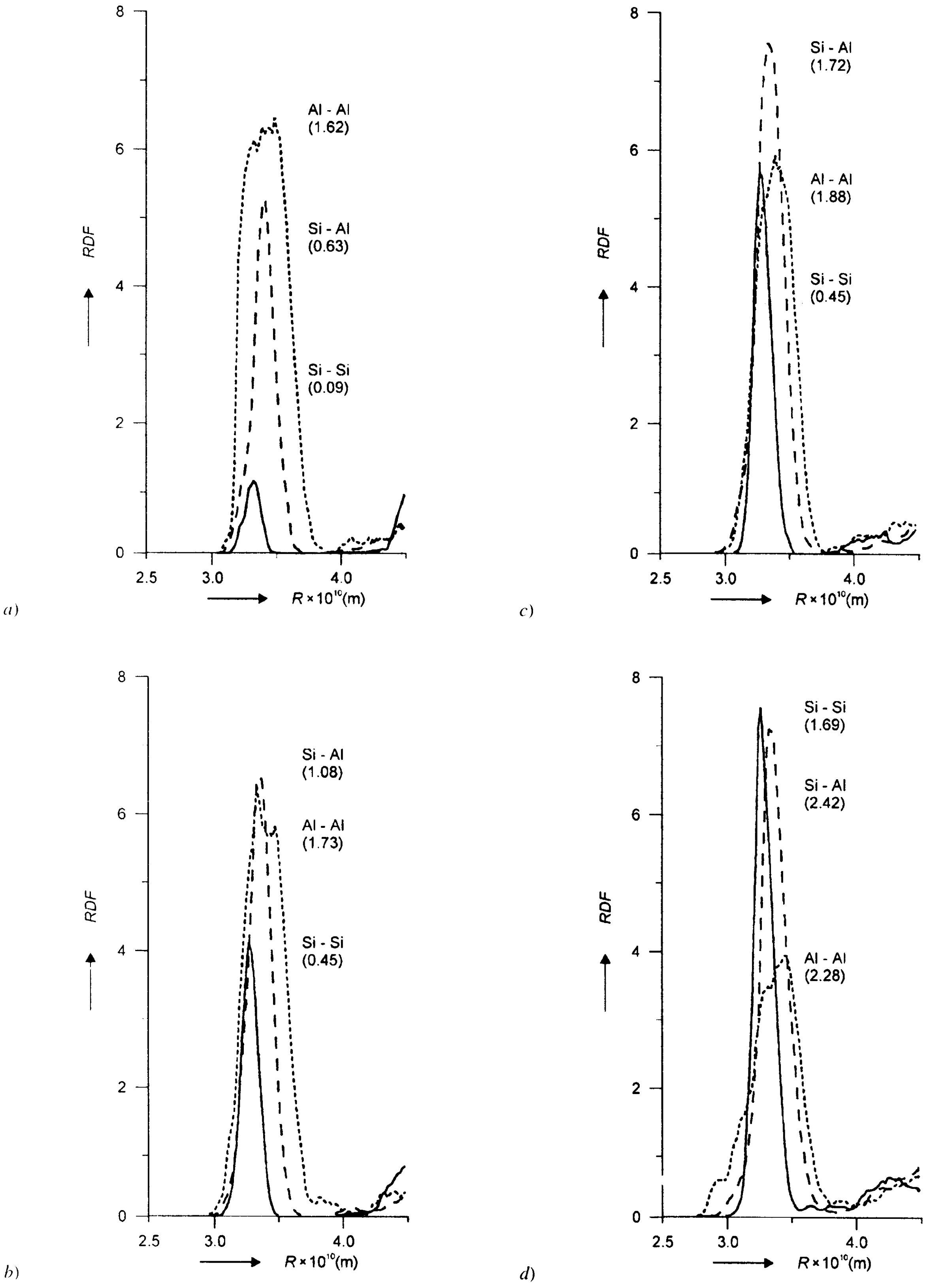

Figure 1. Partial radial distribution functions (RDF) for the MD simulated calcium aluminosilicate systems. ———— Si-Si, – – – – – – Si-Al, ... Al-Al; *a*) system CAS 11, *b*) system CAS 10, *c*) system CAS 5, *d*) system CAS 2. The numbers in parentheses are the respective coordination numbers obtained by integration of the RDFs.

and Al-Al pairs for each composition. For the system CAS11, the Si-Si peak is very small because of almost one half of the Si atoms being bound in isolated SiO_4 tetrahedra and the majority of the rest occupying the terminal sites of aluminosilicate chains. AlO_4 tetrahedra with a varying number of BO prefer the middle sites of the chains. In this system, there are present structural motifs of the crystalline phases that would gradually crystallize from the melt, namely the free SiO_4 tetrahedra of dicalcium silicate and the chains of AlO_4 tetrahedra found in tricalcium aluminate as 6-membered rings. Hence, the simulated structure clearly reflects the tendency for crystallization, since this composition is out of the glass forming region.

As the polymerization degree increases in the systems CAS10-CAS2, the Si and Al atoms are more uniformly distributed throughout aluminosilicate polyanions. At the same time, the principle of occupation of the most branched sites by aluminium is preserved. Nevertheless, even for the CAS2 system (anorthite composition), this distribution cannot be considered statistically random as reported by Scamehorn [9] for simulation results for the same composition. The Si-O-Al bridges are predominant, but the number of Al-O-Al bridges is only slightly lower.

It is difficult to decide whether these deviations from the structural interpretation of experimental data for real systems result from unrealistic energetics, the quite simple form of the PPF set used for the simulations, or from the high degree of disorder which characterizes the melt structure at high temperature and is preserved at the enormous simulation quenching ates. The lower density of the simulated systems compared to real ones will have also some influence on their structure.

CONCLUSIONS

The MD simulated calcium aluminosilicate systems, with constant ratio $Al/Si = 1$ and different polymerization degree for the polyanions, show the predominant tetrahedral coordination of the network forming Si and Al atoms, while some other coordinations (3 and 5) are also present, mainly in more polymerized systems. Al atoms are always found in the most branched sites of the polyanions, unlike Si atoms which are predominantly coordinated by NBOs. The negative charges of the $(AlO_4)^-$ groups are compensated in more polymerized systems not only by the Ca^{2+} cations but also by oxygen atoms bound to three network forming atoms.

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ŠTRUKTÚRA SIMULOVANÝCH HLINITOKREMIČITANOVÝCH SYSTÉMOV

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Molekulovo dynamické simulácie systému $CaO-Al_2O_3-SiO_2$ ukázali na zásadne rozdielnu štruktúrnu pozíciu atómov Si a Al pri tvorbe hlinitokremičitanových polyaniónov. Uvedený rozdiel je výraznejší pri nižších priemerných polymerizačných stupňoch. V sústavách s vyššou koncentráciou nemostikových kyslíkov sa hlinité katióny preferenčne umiestňujú do rozvetvených štruktúrnych pozícií, zatiaľ čo atómy Si sú zvačša situované na okraji hlinitokremičitanových polyaniónov. So zvyšovaním polymerizačného stupňa sa v simulovaných systémoch pozoruje zvýšený výskyt (1-5%) 5-koordinovaných štruktúrnych jednotiek TO_5, kde T=Si,Al. V systémoch s vysokým polymerizačným stupňom sa pozorovala zvýšená koncentrácia (až 7%) tzv. triklastrov TO_3, tj. trojvazbových atómov kyslíka viazaných k atómom Si a Al.