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PREDICTIONS ON THE FORMATION AND BOND PERFORMANCE OF SOME ETTRINGITES BY A QUANTUM CHEMISTRY METHOD

Cheng Xin, Yu Jinghua, Liu Futian, Yue Yunlong and Chang Jun
Department of Materials Science and Engineering,
Shandong Building Materials Institute, Jinan, Shandong, 250022 P.R.China

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ABSTRACT

Mg-, Zn- and Mn-bearing ettringites are studied by a computational quantum chemistry method, the self-consistent-field discrete variation X_α method(SCF-DV-X_α). Their bond order, population, net charge and covalent bond order are obtained. Because the bond order of the O_5 atom in Mg-bearing ettringite is negative, and the net charges of O_5, O_7, and O_{11} atoms are positive, the Mg-bearing ettringite does not exist by the structure of ettringite. The bond orders of Zn and Mn atoms, and the covalent bond order of Zn-O and Mn-O bond in Zn- and Mn-bearing ettringites are higher than these of Ca and Ca-O bond in ettringite, so we can predict that the bond of Zn- and Mn-bearing ettringites is higher than ettringite. © *1997 Elsevier Science Ltd*

Introduction

Quantum chemistry is used to study the structure of substances at the level of molecules, atoms and electrons. Applying quantum chemistry in cement science can solve some problems that are not settled by the conventional theories and methods.

Feng Xiuji (1) first used quantum chemistry to the field of cement chemistry in which the structure and performance of β-C_2S and γ-C_2S are studied. The fundamental reason that the hydraulic reactivity of β-C_2S is higher than that of γ-C_2S is that the Ca-O bond of β-C_2S is weaker than that of γ-C_2S. With this method Cheng Xin (2) studied the hydraulic reactivity of the some minerals in $Ca_2Fe_{2-x}Al_xO_5$ system, which determined the reason that the hydraulic reactivity of $Ca_2Fe_{2-x}Al_xO_5$ system enhances with the adding of Al content. The hydraulic reactivity of $Ca_{4-x-y}Sr_xBa_y Al_6SO_{16}$ system are also studied (2). Cheng Xin (2) also studied the bond performance of Sr- and Ba-bearing ettringites in which the results are corresponding to their mechanics strength, so the relation between microstructure and macro-performance is founded. Li Beixing (3) investigated the hydraulic reactivity of some calcium aluminates. All the above studies are well in accordance with the experimental results. In this paper we are devoted to predict the formation and bond performance of Mg-, Zn- and Mn-bearing ettringites with the self-consistent-field discrete variation X_α method (SCF-DV-X_α), which is an initial step for the design of cement materials.

Quantum Chemistry Method

The key question of computational quantum chemistry is to answer Schrödinger equation

$$H\Psi = E\Psi$$

For general molecular system, answering Schrödinger equation is too difficult to be explained exactly, so some assumptions must be adopted: non-relativity, Born-Oppenheimer and orbits assumptions. Applying calculus principle the Schrödinger equation is developed to answer the Schrödinger equation of a single electron

$$F\psi_i = \varepsilon_i\psi_i$$

where F is Hartree-Fock operator, ψ_i is the wave function of electron i, and ε_i is the energy of electron i. this equation is called as Hartree-Fock equation, which can be explained by self-consistent method. The self-consistent method by Fock was extensively applied in the computation of molecular orbits. No matter what method (conventional orbits or X_α) is, it is all begun from Hartree-Fock equation. Molecular orbits are considered as the linear combination of atomic orbits (LCAO) in the conventional method of molecular orbits. Under this assumption Hartree-Fock equation is exchanged to Roothaan equation. Without any other assumptions the explanation of Roothaan equation is called the famous *ab initio* method. In multi-atoms molecular systems, the computation of Roothaan equation includes much center integrals in which some integrals (matrix elements) can not be solved exactly or waste too much times. Up to now the *ab initio* method has been mainly used in small molecules composed by lighter atoms, such as H, OH, HCN and so on. For large molecules or heavier atoms, some semi-empirical methods, which replace some matrix units by experienced parameters, are frequently adopted. But their exactness is not satisfied the higher precise studies.

Another method for large molecular systems with heavier atoms is X_α method. X means the exchange energy between electrons, and α is a parameter of exchange energy functional. In this method the exchange energy is considered as statistical mean approximations. The localized functional of exchange energy is deduced by wave functions of free electrons

$$V_{ex} = 3\alpha[(3/8\pi)\cdot \rho(r)]^{1/3}$$

where V_{ex} is exchange energy between electrons, α is adjustable from 2/3 to 1 in general, and $\rho(r)$ is the charge density. Under above assumption, Hatree-Fock equation is exchanged to X_α equation

$$[-1/2\ \nabla^2 + \nabla_c + V_{ex}]\ \psi_i = \varepsilon_i\psi_i$$

where $-1/2\ \nabla^2$ is the kinetic energy operator, ∇_c is the Coulomb potential energy operator, and V_{ex} is the exchange energy operator. Owing to this assumption, the multi-center integrals is avoided, and the computational quantities are about the one hundredth of *ab initio* method. Sometimes the accuracy is well matched that of *ab initio* method.

The SCF-DV-X_α method used in this paper was advanced from 1976 to 1982 by D.E. Ellis (4). The main principle is: In a three-dimensional grid, a series of discrete points are selected. Error functions are determined with the approximate solutions of relevant equations of single particles. By the calculus on proper parameters of variations, and making the error functions minimums to all the sampling points, then the secular equation is obtained.

The center problem of computations is to answer Hartree-Fock equation of single particle

$$\mathbf{F}\psi_i = \varepsilon_i\psi_i$$

where

$$\mathbf{F} = [-1/2\, \nabla^2 + \mathbf{V}_n + \mathbf{V}_c + \mathbf{V}_{ex}]$$

where $\mathbf{V}_n$ is the attraction of nuclei on electrons, $\mathbf{V}_c$ is the repelling between electrons. Applying LCAO method, selecting proper error function, adopting Diophantus formula of multi-dimension numerical integrates and making minimums, the secular equation (matrix form) is obtained:

$$\mathbf{HC} = \varepsilon\mathbf{SC}$$

Where **H** is Hamilton matrix, **S** is overlap matrix. This secular equation can be explained by conventional method, and matrix elements by discrete variation method. That is, the matrix

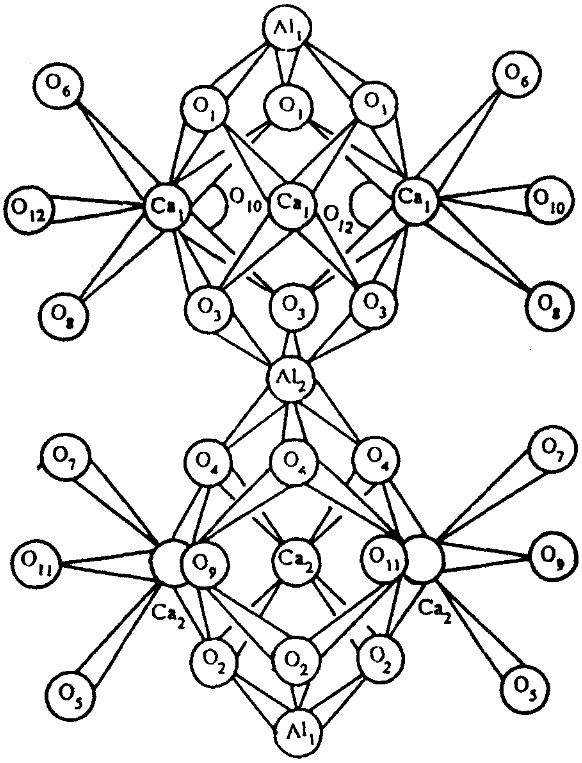

FIG. 1.
The structure sketch of ettringite (6).

TABLE 1

Coordinates of $Al_2Ca(Mg, Zn\ and\ Mn)_3(1)O_{15}$ for Computation(a.u.)

Atoms	x	y	z
Al_1	0	0	20.302
Al_2	0	0	10.151
Ca(Mg,Zn and Mn)$_1$	0.170	-4.023	5.076
O_1	2.469	-1.229	18.191
O_3	2.682	-1.639	12.384
O_6	0.017	-7.280	18.597
O_8	-0.064	-7.361	11.694
O_{12}	4.278	-6.087	15.025

elements of **H** and **S** are summed by sampling points, not integrated. In addition, in the computation, two center charges distributions are decomposed into one center charges distributions. This method has been widely used in studying molecules, clusters, solids and so on, and much satisfied results are obtained.

Computation and Discussions

The computational program of SCF-DV-X_α method is also advanced by D.E. Ellis. It was improved to be applied in a CYBER-930 computer in this paper. The program includes three sub-programs called DIRAC, PROJEC and MOL51 program. MOL51 is the main computation program. The computation of three programs needs much raw data, including the inherent parameters and coordinates of each class atom in the computational models. DIRAC program is to determine the atomic base functions. PROJEC program calculates the base of symmetry orbits. Then MOL51 completes all the computation. By an atomic base function the charge density $\rho(r)$ can be gained, then answering secular equation can obtain a new $\rho(r)$. This is one iteration. Again and again, until the convergence is made, the iteration is over, and the computation is ended. As a general molecule, iterating 20-30 times is needed. For some large molecules, it ineeds more than 50 times. The α values of Ca, Sr, Ba, Al and O are 0.71894, 0.70504, 0.69927, 0.72853 and 0.74447 respectively (5).

TABLE 2

Coordinates of $Al_2Ca(Mg, Zn\ and\ Mn)_3(2)O_{15}$ for Computation(a.u.)

Atoms	x	y	z
Al_1	0	0	10.151
Al_2	0	0	10.151
Ca(Mg,Zn and Mn)$_2$	-0.129	4.023	5.076
O_2	2.488	1.437	2.314
O_4	2.285	1.319	8.040
O_5	0.000	7.406	1.909
O_7	-0.064	-7.361	11.694
O_{11}	4.775	5.885	5.115

TABLE 3

Bond Order, Population and Net Charge of
$Al_2Ca_3(1)O_{15}$, $Al_2Ca_3(2)O_{15}$, $Al_2Mg_3(1)O_{15}$ and $Al_2Mg_3(2)O_{15}$

Atoms	Bond order	Population	Net charge	Atoms	Bond order	Population	Net charge
$Al_2Ca_3(1)O_{15}$				$Al_2Mg_3(1)O_{15}$			
Al_1	0.2282	2.6386	0.3632	Al_1	0.2151	2.6295	0.3705
Al_2	0.1689	2.5345	0.4655	Al_2	0.1861	2.3233	0.6767
Ca_1	0.5134	0.8416	1.1584	Mg_1	0.8725	1.2791	0.7209
O_1	0.4502	2.3390	-0.3390	O_1	0.4471	2.2819	-0.2819
O_3	0.3167	2.4705	-0.4705	O_3	0.4427	2.3213	-0.3213
O_6	0.1682	2.1166	-0.1166	O_6	0.1536	2.1268	-0.1268
O_8	0.0556	2.1554	-0.1554	O_8	0.1756	2.1736	-0.1736
O_{12}	0.1617	2.2931	-0.2931	O_{12}	0.2571	2.1304	-0.1304
$Al_2Ca_3(2)O_{15}$				$Al_2Mg_3(2)O_{15}$			
Al_1	0.1884	2.4161	0.5839	Al_1	0.1364	2.0836	0.9164
Al_2	0.2013	2.6142	0.3858	Al_2	0.1280	2.2060	0.7940
Ca_2	0.4851	1.0014	1.9986	Mg_2	0.3943	1.0415	0.9585
O_2	0.3517	2.4716	-0.4716	O_2	0.3360	2.3358	-0.3358
O_4	0.4421	2.3762	-0.3762	O_4	0.3527	2.4082	-0.4082
O_5	0.0386	2.1613	-0.1613	O_5	-0.0172	1.3890	0.6110
O_7	0.1727	2.2629	-0.2629	O_7	0.1107	1.3912	0.6088
O_{11}	0.1849	2.0519	-0.0519	O_{11}	0.0930	1.3432	0.6568

The structure parameters of ettringite are from Moore and Taylor (6). Space group is P31c; Unit cell parameter is a = 11.26Å, c = 21.48Å. In the structure analysis of Moore and Taylor, the H_2O and OH^- in position is approximately considered as O atom. We adopted this approximation in the quantum chemistry studies. From Fig. 1, the basic structure units of ettringite are composed of two cages combined and shared by Al_1 and Al_2. Considering the characteristics of computational programs, two cages are divided to two structure models with C_3 symmetry type. The one is the upper part of the sketch (see Fig. 1), containing one Al_1 (the above Al_1 of Fig. 1), one Al_2, three Ca_1, three O_1, three O_3, three O_6, three O_8 and three O_{12}. The other is the lower part of sketch (see Fig. 1), containing one Al_1 (the below Al_1 of Fig. 1), one Al_2, three Ca_2, three O_2, three O_4, three O_5, three O_7 and three O_{11}. They are expressed as $Al_2Ca_3(1)O_{15}$ and Al_2Ca_3 $(2)O_{15}$.The structures with Mg, Zn and Mn are considered as the replacement of Ca in ettringite by Mg, Zn and Mn partly, and the models are expressed as $Al_2Mg_3(1)O_{15}$, $Al_2Mg_3(2)O_{15}$, $Al_2Zn_3(1)O_{15}$ $Al_2Zn_3(2)O_{15}$, $Al_2Mn_3(1)O_{15}$ and $Al_2Mn_3(2)O_{15}$ respectively. The computational coordinates of two type models are shown in Tables 1 and 2. According to the regulations of computational program, the coordinates and some inherent parameters of atoms are imported into a CYBER-930 computer. After computing 50 repeating times the convergence is made.

The bond order, population and net charge of atoms in $Al_2Ca_3(1)O_{15}$, $Al_2Ca_3(2)O_{15}$, $Al_2Mg_3(1)O_{15}$, $Al_2Mg_3(2)O_{15}$, $Al_2Zn_3(1)O_{15}$ $Al_2Zn_3(2)O_{15}$, $Al_2Mn_3(1)O_{15}$ and $Al_2Mn_3(2)O_{15}$ are shown in Tables 3 and 4; the covalent bond orders of them are in Tables 5 and 6, respectively. In the four minerals, the bond order and the covalent bond order of Al are almost the

TABLE 4

Bond Order, Population and Net Charge of
$Al_2Zn_3(1)O_{15}$, $Al_2Zn_3(2)O_{15}$, $Al_2Mn(1)O_{15}$ and $Al_2Mn(2)O_{15}$

Atoms	Bond order	Population	Net charge	Atoms	Bond order	Population	Net charge
	$Al_2Zn_3(1)O_{15}$				$Al_2Mn_3(1)O_{15}$		
Al_1	0.2007	2.5765	0.4235	Al_1	0.2048	2.5798	0.4202
Al_2	0.1797	2.5498	0.4502	Al_2	0.1750	2.4678	0.5322
Zn_1	0.8609	1.5047	0.4953	Mn_1	1.2127	1.2753	0.7247
O_1	0.3898	2.2868	-0.2868	O_1	0.4608	2.2615	-0.2615
O_3	0.2969	2.2799	-0.2799	O_3	0.3589	2.3177	-0.3177
O_6	0.2783	2.0731	-0.0731	O_6	0.3643	2.1727	-0.1727
O_8	0.2639	2.0435	-0.0435	O_8	0.1643	2.1194	-0.1194
O_{12}	0.0691	2.1034	-0.1034	O_{12}	0.2169	2.1709	-0.1709
	$Al_2Zn_3(2)O_{15}$				$Al_2Mn_3(2)O_{15}$		
Al_1	0.1893	2.5687	0.4313	Al_1	0.1775	2.3666	0.6394
Al_2	0.1745	2.5510	0.4490	Al_2	0.1673	2.6226	0.3774
Zn_2	0.8271	1.5269	0.4731	Mn_2	1.0319	1.5142	0.4858
O_2	0.4236	2.3179	-0.3179	O_2	0.4622	2.2866	-0.2866
O_4	0.3535	2.2975	-0.2975	O_4	0.3793	2.3151	-0.3151
O_5	0.1797	2.1290	-0.1290	O_5	0.3765	2.0761	-0.0761
O_7	0.2817	2.1661	-0.1661	O_7	0.3322	2.1585	-0.1585
O_{11}	0.1363	2.0435	-0.0435	O_{11}	0.1389	2.0116	-0.0116

same, so we can consider that the influence on the difference in the bond combination of them is mainly owing to the replacement of Ca by Mg, Zn and Mn. From Table 3, the bond order of the O_5 atom in Mg-bearing ettringite is negative, and the net charges of O_5, O_7, and O_{11} atoms are positive. So we can consider that the Mg-bearing ettringite does not exist, at least not exist by the structure of ettringite. Zn- and Mn-bearing ettringites are able to be formed. From Table 3, the bond order of Ca in $Al_2Ca_3(1)O_{15}$ and $Al_2Ca_3(2)O_{15}$ are 0.5134 and 0.4851; From Table 4, the bond order of Zn in $Al_2Zn_3(1)O_{15}$ and $Al_2Zn_3(2)O_{15}$ are 0.8609 and 0.8271; From Table 4 the bond orders of Mnin $Al_2Mn_3(1)O_{15}$ and $Al_2Mn_3(2)O_{15}$ are 1.2127 and 1.0319, respectively. From Tables 5 and 6, the average covalent bond order of Ca-O bond in $Al_2Ca_3(1)O_{15}$ and $Al_2Ca_3(2)O_{15}$ are 0.1279 and 0.1245; Zn-O bond in $Al_2Zn_3(1)O_{15}$ and $Al_2Zn_3(2)O_{15}$ are 0.1761 and 0.1797; Mn-O bond in $Al_2Mn_3(1)O_{15}$ and $Al_2Mn_3(2)O_{15}$ are 0.2433 and 0.2176 respectively. The higher bond order and covalent bond order are, the higher bond combination is. Zn- and Mn-bearing ettringites are of higher bond combination than ettringite is, and Mn-bearing ettringite has the highest bond combination.

Conclusions

The bond order, population, net charge and covalent bond order of four ettringite phases are obtained through computation of quantum chemistry.

The Mg-bearing ettringite with the structure of ettringite does not exist. The difference of bond combination in three minerals is caused by the variation of Ca, Zn and Mn.

TABLE 5

Covalent Bond Order of $Al_2Ca_3(1)O_{15}$, $Al_2Ca_3(2)O_{15}$, $Al_2Mg_3(1)O_{15}$ and $Al_2Mg_3(2)O_{15}$

$Al_2Ca_3(1)O_{15}$		$Al_2Ca_3(2)O_{15}$	
$Ca\text{-}O_1(6)$	1.0194	$Ca\text{-}O_2(6)$	0.7715
$Ca\text{-}O_3(6)$	0.7570	$Ca\text{-}O_4(6)$	1.0331
$Ca\text{-}O_6(3)$	0.2915	$Ca\text{-}O_5(3)$	0.1514
$Ca\text{-}O_8(3)$	0.2431	$Ca\text{-}O_7(3)$	0.4048
$Ca\text{-}O_{12}(3)$	0.3724	$Ca\text{-}O_{11}(3)$	0.2527
Ave.	0.1279	Ave.	0.1245
$Al_1\text{-}O_1(3)$	0.8141	$Al_1\text{-}O_2(3)$	0.6643
$Al_1\text{-}O_3(3)$	0.6389	$Al_2\text{-}O_4(3)$	0.7709
Ave.	0.2422	Ave.	0.2392
$Al_2Mg_3(1)O_{15}$		$Al_2Mg_3(2)O_{15}$	
$Mg\text{-}O_1(6)$	1.1269	$Mg\text{-}O_2(6)$	1.0824
$Mg\text{-}O_3(6)$	1.1133	$Mg\text{-}O_4(6)$	1.0750
$Mg\text{-}O_6(3)$	0.5440	$Mg\text{-}O_5(3)$	0.0086
$Mg\text{-}O_8(3)$	0.5534	$Mg\text{-}O_7(3)$	0.2454
$Mg\text{-}O_{12}(3)$	0.6052	$Mg\text{-}O_{11}(3)$	0.1429
Ave.	0.1878	Ave.	0.1208
$Al_1\text{-}O_1(3)$	0.7609	$Al_1\text{-}O_2(3)$	0.5189
$Al_1\text{-}O_3(3)$	0.6552	$Al_2\text{-}O_4(3)$	0.5497
Ave.	0.2360	Ave.	0.1781

(6)-six bonds (3)-three bonds

TABLE 6

Covalent Bond Order of $Al_2Zn_3(1)O_{15}$, $Al_2Zn_3(2)O_{15}$, $Al_2Mn_3(1)O_{15}$ and $Al_2Mn_3(2)O_{15}$

$Al_2Zn_3(1)O_{15}$		$Al_2Zn_3(2)O_{15}$	
$Zn\text{-}O_1(6)$	0.9915	$Zn\text{-}O_2(6)$	1.2306
$Zn\text{-}O_3(6)$	0.8307	$Zn\text{-}O_4(6)$	0.9225
$Zn\text{-}O_6(3)$	0.8091	$Zn\text{-}O_5(3)$	0.5987
$Zn\text{-}O_8(3)$	0.7473	$Zn\text{-}O_7(3)$	0.8554
$Zn\text{-}O_{12}(3)$	0.3207	$Zn\text{-}O_{11}(3)$	0.1664
Ave.	0.1761	Ave.	0.1797
$Al_1\text{-}O_1(3)$	0.7244	$Al_1\text{-}O_2(3)$	0.6566
$Al_1\text{-}O_3(3)$	0.6170	$Al_2\text{-}O_4(3)$	0.6520
Ave.	0.2236	Ave.	0.2181
$Al_2Mn_3(1)O_{15}$		$Al_2Mn_3(2)O_{15}$	
$Mn\text{-}O_1(6)$	1.3836	$Mn\text{-}O_2(6)$	1.3944
$Mn\text{-}O_3(6)$	1.1764	$Mn\text{-}O_4(6)$	1.0344
$Mn\text{-}O_6(3)$	1.1269	$Mn\text{-}O_5(3)$	0.9888
$Mn\text{-}O_8(3)$	0.6033	$Mn\text{-}O_7(3)$	0.8927
$Mn\text{-}O_{12}(3)$	0.8181	$Mn\text{-}O_{11}(3)$	0.2588
Ave.	0.2433	Ave.	0.2176
$Al_1\text{-}O_1(3)$	0.7657	$Al_1\text{-}O_2(3)$	0.6405
$Al_1\text{-}O_3(3)$	0.6601	$Al_2\text{-}O_4(3)$	0.6495
Ave.	0.2376	Ave.	0.2125

(6)-six bonds (3)-three bonds

Zn- and Mn-bearing ettringites have higher bond combination than ettringite does, and Mn-bearing ettringite has the highest.

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