Hydrolysis during hydration of anhydrous calcium sulfosilicate

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ABSTRACT

The results of a comprehensive study of the liquid and solid phases of hydrating anhydrous minerals allow us to draw the following conclusion in dilute suspensions, highly basic hydrates are formed in the earliest periods of hydration and over time due to the formation of a dense shell consisting of hydrolysis products primary hydrates that are more stable under these conditions. The presence of CaSO4 in a mixture with β -C2S significantly accelerates the main period of its hydration and promotes better crystallization of neoplasms.

Keywords: sulfa cement, sulfa silicate, hydration, of sulfa silicates, hydro sulfa silicate minerals, congruent composition, molar ratio, physic-chemical processes.

1. Introduction.

To understand the hardening process and control it, the features of the hydration of sulfa silicates were studied [1]. The presence in nature of hydro sulfa silicate minerals-trauma cites and reunites /191/ causes interest in studying the interaction of anhydrous calcium sulfa silicate with water under normal conditions.

To clarify the properties and composition of the hydrate phases formed, the kinetics of dissolution and hydrolysis processes during hydration of calcium sulfa silicate was studied. The obtained data are used to explain the physic-chemical processes of hardening of sulfated cements, in particular, sulfa cements. For the experiments, dilute suspensions (0.1-0.5%) containing no CO2 were taken, taking into account the complete dissolution of CaCO4. It was found that in the absence of carbon dioxide, the hydrolysis of β-C2S in dilute aqueous suspensions is very slow. The congruent composition of the solutions persists for a long time (7-28 days), depending on the concentration of the suspension (Table 1), then the silica gel drops out, and the earlier the greater the SiO2 content in the solution. At the same time, the amount of soluble CaO also increases, but even after 10 months it does not exceed 0.34 g /l. Consequently, the main phase in the system is 2CaO*SiO2•nH2O with a small admixture of CS•pN2O, the study of the composition of the liquid phase of aqueous suspensions from β-C2S over various time periods showed that in the absence of CO2 at any concentrations and temperature of 20-25 ° C, congruent dissolution of C2S (0.22 g in 1 l) occurs. But the duration of the stable state of the suspension depends on its concentration.

2. The purpose of the research:

Hydrolysis of C2S in dilute aqueous suspensions is accompanied by an increase in the concentration of CaO and a decrease in SiO2. In more concentrated suspensions, the hydrolysis process manifests itself much earlier. So, in 0.5% solutions, after 25 days, the content of CaO increases by more than 2 times, and SiO2 decreases by 7 times; the molar ratio of CaO / SiO2 is 34.53. In 0.4% suspension, this process is slower; the molar ratio increases to only 3.76. In more dilute suspensions (0.2% and 0.1%), the stable state is maintained up to 1-10 months.

Table 1

Change in the composition of the liquid phase in aqueous suspensions of β-C2S (g/l) depending on its concentration and hydration time

Hydration time	CaO	SiO_2	C:S	CaO	SiO_2	C:S
	T:J=1:200				T:J=1:250	
1 h	0,1400	0,0780	1,92	0,1310	0,0730	1,92
3 h	0,1400	0,0780	1,93	0,1360	0,0755	1,93
6 h	0,1445	0,0790	1,96	0,1360	0,0780	1,87
12 h	0,1445	0,0790	1,95	0,1355	0,0780	1,86
24 h	0,1450	0,0760	2,04	0,1360	0,0780	1,87
3 day	0,1490	0,0780	2,05	0,1355	0,0810	1,81
7 day	0,1500	0,0795	2,02	0,1380	0,0820	1,77
28 day	0,3385	0,0105	34,53	0,1695	0,0480	3,76
3 month	-	-	-	0,3016	0,0080	38,47
10 month	-	-	-	0,3386	0,0088	40,20
	T:J=1:500				T:J=1:1000	
1 h	0,0979	0,0499	2,09	0,0978	0,0532	1,96
3 h	0,1258	0,0614	2,19	0,0979	0,0547	1,90
6 h	0,1248	0,0624	2,14	0,1072	0,0588	1,98
12 h	0,1212	0,0665	1,95	0,1072	0,0588	1,95
24 h	0,1218	0,0632	2,06	0,1072	0,0588	1,95
3 day	0,1212	0,0665	1,95	0,1119	0,0582	2,00
7 day	1,1258	0,0664	1,92	0,1119	0,0616	1,91
28 day	0,1272	0,0710	1,91	0,1119	0,0615	1,90
3 month	0,2010	0,0110	17,98	0,1119	0,0632	1,85

10 month	0,2138	0,0110	20,84	0,1119	0,0632	1,85

In preparations from C2S in 0.1% suspension after 10 months of storage, the gel-like product turns into fine-grained with a large number of needle crystals (NSR = 1.573), observed even under a conventional light microscope and corresponding to low-base calcium hydro silicate. The main fine-grained mass has NSR = 1.620. Complete hydration of C2S after 10 months is not achieved even in 0.2% suspension (d=2.73 and 2.76 A), which is difficult to detect using microscopic and thermo graphic analyses. Mainly formed C2SN2 (d=9.7, 3.05, 2.87, 2.19 A) and gyro lite Ca4(Si6O15)•(OH)2*ZN2O (d=6,6, 3,73, 3,35, 3,19, 2,92, 2,28 A). With an increase in the concentration of the suspension, the proportion of the non-hydrated part of the mineral increases. Thus, at 0.4% concentration, the C2S lines are planted more clearly (d=2.73, 2.76, 2.60 A), and the C2SH2 lines are weaker, some of them are covered with gyro lite lines (d=6,6, 3,84, 3,37, 3,15, 2,22, 2,11, 2,04, 1,88, 1,77, 1,48, 1,42 A).

At concentrations corresponding to the cement dough, C2SH2 is less crystallized and its lines are obscured by the lines of the non-hydrated part of the mineral.

At high concentrations of suspensions from C2S hydration products, aggregates with higher refractive indices and polar inability are sometimes detected. This indicates the presence of non-hydrated C2S grains coated with neoplasms. After 10 months of storage, these aggregates are not detected under the microscope. At lower concentrations (0.1%), complete hydration of the starting substance occurs, the doublet lines characteristic of C2S disappear, the C2SH2 lines are clearly outlined (d= 9.7, 3.05, 2.12, 2.06 A); the gyro lite phase is partially present (d=6.5 and 3.25 A).

The presence of anhydrite in a mixture of C2S and CaCO4 does not significantly affect the phase composition of the hydration products, but accelerates the reaction rate, as can be seen from the radiographs[2-4].

In 0.5-0.4% sulfa silicate suspensions, congruent decomposition corresponding to the composition of c5s2Ŝ is observed only in the first hours of hydration (1-6 hours), in more dilute ones this state persists longer (Table.2). By day 28, the solubility of CaSO4 increases to 0.90-0.24 g / l, 86-64% of its total content in 0.1-0.5% suspensions passes into the solution.

Anhydrite in a mixture consisting of β-C2S and burnt CaSO4 (Table.3), dissolves more intensively. For example, in the liquid phase of a 0.2% suspension after 28 days of storage, its solubility was 95.6%.

Our data showed that burnt at 1250°With CaSO4 (for 1 hour) by 28 days at room temperature and a suspension of 0.2 g in 100 ml of water completely passes into an aqueous solution. The solubility of CaSO4 by this time was 2.02 g/l. After 6 hours, 45.0% of the taken sample passes into the solution (0.2 g per 100 ml), the concentration of CaSO4 reaches 0.9 g / l. The same concentration of CaSO4 by this time is observed at a weight of 0.5 g per 100 ml. Thus, free anhydrite dissolves approximately 3.5 times faster than the bound sulfa silicate.

Table 2

Change in the composition of the liquid phase in aqueous suspensions 2(C2S•*CS (g/l) depending on its concentration and hydration time

Hydration time	CaO$_{общ}$	SiO	SO_3	$CaO:SiO_2:CaSO_4$
	T:J=1:200			
1 h	0,1399	0,0600	0,0400	2,00:1,00:0,50
3 h	0,3002	0,0695	0,2647	1,76:1,00:2,86
6 h	0,3373	0,0694	0,3144	1,80:1,00:3,40
12 h	0,4168	0,0495	0,3715	3,40:1,00:5,64
24 h	0,4498	0,0478	0,3994	3,79:1,00:6,26
3 day	0,5545	0,0144	0,4600	17,40:1,00:23,97

7 day	0,6552	0,0079	0,5073	40,79:1,00:48,70
28 day	0,7681	0,0079	0,5293	54,03:1,00:50,85
3 month	-	-	-	-
10 month	-	-	-	-
	T:J=1:250			
1 h	0,1623	0,0696	0,0464	2,00:1,00:0,50
3 h	0,2904	0,0760	0,2306	1,82:1,00:2,23
6 h	0,3094	0,0725	0,2660	1,82:1,00:2,76
12 h	0,3567	0,0580	0,3003	2,71:1,00:3,90
24 h	0,3980	0,0550	0,3337	3,17:1,00:4,59
3 day	0,4873	0,0160	0,4044	13,68:1,00:18,98
7 day	0,5347	0,0091	0,4030	29,80:1,00:33,30
28 day	0,6137	0,0092	0,4706	38,92:1,00:36,95
3 month	0,6760	0,0086	0,4860	41,95:1,00:42,85
10 month	0,7298	0,0073	0,4868	57,99:1,00:50,00
	T:J=1:500			
1 h	0,1431	0,0598	0,0416	2,04:1,00:0,52
3 h	0,1456	0,0631	0,0470	1,97:1,00:0,49
6 h	0,1455	0,0624	0,0416	2,00:1,00:0,50
12 h	0,2564	0,0631	0,2090	1,86:1,00:2,48
24 h	0,2949	0,0448	0,2138	3,44:1,00:3,58
3 day	0,3172	0,0115	0,2240	14,97:1,00:14,60
7 day	0,3590	0,0108	0,2395	19,00:1,00:17,00
28 day	0,3724	0,0105	0,2400	20,30:1,00:16,66
3 month	0,3840	0,0108	0,2535	19,50:1,00:17,62
10 month	0,4200	0,0100	0,2766	23,77:1,00:20,77
	T:J=1:1000			
1 h	0,1053	0,0482	0,0301	1,87:1,00:0,47
3 h	0,1111	0,0482	0,0355	1,93:1,00:0,48
6 h	0,1260	0,0600	0,0360	2,00:1,00:0,50
12 h	0,1865	0,0648	0,1230	1,63:1,00:1,42
24 h	0,1865	0,0649	0,1245	1,64:1,00:1,43
3 day	0,1865	0,0632	0,1315	1,59:1,00:1,56
7 day	0,1938	0,0642	0,1360	1,64:1,00:1,59
28 day	0,1925	0,0635	0,1390	1,60:1,00:1,77
3 month	0,2045	0,0645	0,1500	1,66:1,00:1,75
10 month	0,2014	0,0600	0,1445	1,60:1,00:1,80

Timetable of 3

Amount of CaSO4, transferred c solution (%), (in dependence the temporary hydration, and the concentration of suspensions

Hydration time	$CaSO_4$		$C_2S+CaSO_4$	$2(C_2S)\cdot CaSO_4$			
	Concentration of suspensions, %						
	0,5(5,00)	0,2(2,00)	0,2(0,566)	0,5(1,41)	0,4(1,13)	0,2(0,56)	0,1(0,28)
1 h	15,3	38,15	-	4,81	6,97	12,62	18,28
3 h	16,7	-	-	31,90	34,60	12,69	21,53
6 h	18,1	45,0	35,36	37,90	40,00	12,62	21,86
12 h	22,4	56,52	66,44	44,70	45,10	63,44	74,68

24 h	23,7	59,26	72,50	48,10	50,30	64,90	75,57
3 day	25,7	63,25	80,15	55,3	60,80	68,00	79,14
7 day	40,5	86,3	81,09	61,1	60,60	72,69	81,97
28 day	40,7	100,0	95,60	63,7	67,20	72,00	84,86
3 month	40,7	-	-	-	73,00	77,00	86,00
10 month	-	-	-	-	73,20	83,01	86,50

Note. The content of CaSO4 in minerals and mixtures, g/l, is given in parentheses.

The amount of CaO and SiO2 transferred to the liquid phase from C5S2S is 0.10-0.40 and 0.007-0.076 g/l, respectively. The gel of silicic acid in sulfa silicate suspensions drops out faster than in β-C2S suspensions. So, in 0.5- and 0.4% sulfa silicate suspensions, after 28 days, the CaO content in the solution increases by more than 3, and SiO2 decreases by 9 times. The molar ratio of CaO/SiO2 is 54-58 (this is probably facilitated by the presence of CaSO4). In β-C2S suspensions, the congruent composition persists depending on the concentration for 7-360 days. Silicic acid in sulfa silicate suspensions precipitates at CaO concentrations above 0.22 g/l (Table 2). Perhaps this is due to the presence of the SO42- anion, which can replace part of the silicic acid and enter (up to 5%) into the calcium hydro silicate lattice.

Indistinctly shaped spherule clusters form in the precipitate of the sulfa silicate filtrate, from which elongated prismatic crystals with Ng = 1.625 and NP = 1.618 crystallize over time, which apparently corresponds to calcium hydro sulfa silicate. On the thermo gram, they are characterized by two end effects: at 180 ° C, probably caused by dehydration of the sulfate-containing phase, and at 900 ° C, due to either dehydration or polymorphic transformation of the formed new compound. The radiograph of the sediment formed from C5S2Ŝ differs from the radiograph of the sediment obtained from the C2S filtrate. The precipitate from the C5S2 filtrate is characterized on the X-ray by lines with d=3,77, 2,37, 2,06, 1,89, 1,85, 1,64, 1,51, 1,43 A. Thus, the end effect at 800-900 ° C on the thermo grams of the precipitate obtained from c5s2Ŝ is associated with the restructuring of the crystal structure of the formed compound. With a decrease in the concentration of the suspension, the first end effect shifts to the region of lower temperatures, which, apparently, is associated with the formation of a low-base hydro silicate (exam-effect at 800-900 ° C).

Hydration of c5s2Ŝ in the test initially proceeds with the decomposition of a part of the substance into C2S (d=2,77, 2,73, 2,61, 2,28, 2,17 A) and CŜ (d=3,84, 3,48, 2,85, 1,98, 1,73 A). The part of C2S released from C5S2Ŝ is hydrolyzed to form gyro lite (d=9,56, 3,04, 2,55, 2,42, 2,09, 2,02, 1,89 A), a new phase (d) appears=9,04, 8,38, 7,65, 3,04, 2,17 A), possibly 2(C2S)•MSc*nH2O, and the hydrolysis cS passes into gypsum (d=7.55 and 4.25 A). X-ray images of hydrated C5S2Ŝ in 0.2-0.1% suspensions are almost identical, which is explained by the same phase composition of hydration products, which consist of well-crystallized C2S2 (d=9.70, 3.07, 2.80, 2.06 A). The latter is apparently due to the presence of an insignificant amount of the SO42-ion in its structure [4-7].

The results of a comprehensive study of the liquid and solid phases of hydrating anhydrous minerals allow us to draw the following conclusions.

3. Conclusion:

In dilute suspensions, the induction hydration period of water-free minerals C2S and C5S2Ŝ is lengthened, and the main period is shortened. This makes it possible to observe the processes occurring in the earliest period of interaction of cement with water. Anhydrous minerals pass into the solution congruently to certain lime concentrations (0.11 g/l), then the hydrates are precipitated. Continuous washing of cements during their hydration with water that does not contain CO2 and soluble (aggressive) salts does not lead to complete decomposition of the binder (to the constituent oxides), since the lime content does not reach 0.11 g/l, necessary for the precipitation of dissolved silica. In dilute suspensions, highly basic hydrates are formed in the earliest periods of hydration and over time are hydrolyzed into less basic ones. In cement mortars, they persist for a long time due to the formation of a dense shell consisting of hydrolysis products of primary hydrates, which are more stable under these conditions.

Consequently, the main hydration products in the absence of CO2 at a content of 0.4 g/l CaO and 0.9 g/l CaCO4 in the surrounding water environment are C2S*nH2O and 2(C2S)*MS*pN2O.

The presence of CaSO4 in a mixture with β-C2S significantly accelerates the main period of its hydration and promotes better crystallization of neoplasms.

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