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A.O. Musina, O.O. Sihunov, T.V. Kravchenko, A.O. Hura

THERMODYNAMIC ANALYSIS OF CHEMICAL REACTIONS IN THE SYSTEMS $FeSi-Ca(OH)_2-H_2O$ AND $FeSi_2-Ca(OH)_2-H_2O$

Ukrainian State University of Chemical Technology, Dnipro, Ukraine

The use of thermodynamic analysis in silicate technology is an integral part of scientific research and an important component in the study of hydration processes. Thermodynamic analysis allowed substantiating the path of the processes of mineral binders hydration and the stability of hydrated formations, which affects the strength of the concrete. To investigate the solidification processes, one should consider both the thermodynamics of the real solutions of astringent in water and the thermodynamics of the coexistence of mixed crystalline phases. We carried out the thermodynamic analysis of hydration reactions in the systems $FeSi-Ca(OH)_2-H_2O$ and $FeSi_2-Ca(OH)_2-H_2O$, that are used in the production of cellular gas concretes. We showed that there is a possibility to perform directed synthesis of the mineralogical composition of hydration products in the systems under study. The sequence of the chemical reactions and their temperature dependences are established. The developed theoretical model allows understanding the mechanisms of hydration of astringent and building materials on their basis, in particular in the study of physicochemical processes occurring in aerated concretes, prepared by both autoclave and non-autoclave curing, which contain gas-forming ferrosilicon of different chemical compositions.

Keywords: aerated concrete, ferrosilicon, thermodynamic analysis, lime, hydration, mineral formation, Gibbs energy.

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Introduction

Thermodynamics plays an important role in the development of the theoretical foundation of numerous chemical and physicochemical processes in the construction industry. The application of thermodynamic methods to the analysis of mineralization reactions, especially in high-temperature synthesis and hydration, is well-known and was elucidated in work [1]. Thermodynamic studies are often used for high-temperature reactions [2–7], but literary sources confirm that good results are observed for hydration reactions as well [8–10].

From the thermodynamic point of view, the chemical processes that occur during solidification and the formation of a porous structure in autoclaved aerated concrete have not been sufficiently studied. In this regard, the processes of gas formation and hydration, which occur in autoclaved aerated concrete, where aluminum powder is used as a gasifier, have been investigated. Because of the interaction of the said reagent with alkali and water, hydrogen is formed which aerates the hardening system.

Thermodynamic analysis of chemical reactions of mineral formation in systems containing aluminum powder is described elsewhere [11]. At the same time, calculations were performed for the reaction products, such as cubic calcium hydroaluminate, tri-sulfate form of hydrosulfoaluminate of calcium and hydrogen, which are characteristic of the production of aerated concrete with gypsum.

As for the theoretical studies of the processes of hydration in silicon-containing systems, the determination of the sequence of possible reactions involving ferrosilicon, no information has been found on these issues.

Thus, this study was devoted to the formation of the composition of hydration products in the systems containing aerated concrete where ferrosilicon is used as a gasifier.

Results and discussion

The following products of the hydration reaction were considered in thus work: calcium hydrosilicates as tobermorite ($5CaO{\cdot}6SiO_2{\cdot}5.5H_2O$), foshagite

($4CaO\cdot 3SiO_2\cdot 1.5H_2O$), xonotlite ($6CaO\cdot 6SiO_2\cdot H2O$), gyrolite ($2CaO\cdot 3SiO_2\cdot 2.5H_2O$), okenite ($CaO\cdot 2SiO_2\cdot 2H_2O$), and hillebrandite ($2CaO\cdot SiO_2\cdot 1.17H_2O$). The calculations of the Gibbs energy of the hydration reactions were carried out in accordance with the principle of the calculation of the composition formulated elsewhere [1].

The main reactions in the system $FeSi-Ca(OH)_2-H_2O$ were considered at the following ratios of calcium hydroxide to ferrosilicon: 1:2; 2:3; 5:6; 6:6; 4:3 and 2:1 (at some constant or close to constant number of moles of water for all reactions):

$Ca(OH)_2:FeSi=1:2$

$$Ca(OH)_2+2FeSi+11.7H_2O\rightarrow \rightarrow 0.2[5CaO\cdot 6SiO_2\cdot 5.5H_2O]+7H_2+ +0.8[H_4SiO_4]+2Fe(OH)_3, \quad (1)$$

$$Ca(OH)_2+2FeSi+11.875H_2O\rightarrow \rightarrow 0.25[4CaO\cdot 3SiO_2\cdot 1.5H_2O]+7H_2+ +1.25[H_4SiO_4]+2Fe(OH)_3, \quad (2)$$

$$Ca(OH)_2+2FeSi+11.17H_2O\rightarrow \rightarrow 0.17[6CaO\cdot 6SiO_2\cdot H_2O]+7H_2+ +H_4SiO_4+2Fe(OH)_3, \quad (3)$$

$$Ca(OH)_2+2FeSi+11.25H_2O\rightarrow \rightarrow 0.5[2CaO\cdot 3SiO_2\cdot 2.5H_2O]+7H_2+ +0.5[H_4SiO_4]+2Fe(OH)_3, \quad (4)$$

$$Ca(OH)_2+2FeSi+11H_2O\rightarrow \rightarrow CaO\cdot 2SiO_2\cdot 2H_2O+7H_2+2Fe(OH)_3, \quad (5)$$

$$Ca(OH)_2+2FeSi+12.585H_2O\rightarrow \rightarrow 0.5[2CaO\cdot SiO_2\cdot 1.17H_2O]+7H_2+ +1.5[H_4SiO_4]+2Fe(OH)_3, \quad (6)$$

$Ca(OH)_2:FeSi=2:3$

$$2Ca(OH)_2+3FeSi+16.4H_2O\rightarrow \rightarrow 0.4[5CaO\cdot 6SiO_2\cdot 5.5H_2O]+10.5H_2+ +0.6[H_4SiO_4]+3Fe(OH)_3, \quad (7)$$

$$2Ca(OH)_2+3FeSi+16.75H_2O\rightarrow \rightarrow 0.5[4CaO\cdot 3SiO_2\cdot 1.5H_2O]+10.5H_2+ +1.5[H_4SiO_4]+3Fe(OH)_3, \quad (8)$$

$$2Ca(OH)_2+3FeSi+15.33H_2O\rightarrow \rightarrow 0.33[6CaO\cdot 6SiO_2\cdot H_2O]+10.5H_2+ +H_4SiO_4+3Fe(OH)_3, \quad (9)$$

$$2Ca(OH)_2+3FeSi+15.5H_2O\rightarrow \rightarrow 2CaO\cdot 3SiO_2\cdot 2.5H_2O+10.5H_2+3Fe(OH)_3, \quad (10)$$

$$2Ca(OH)_2+3FeSi+16.5H_2O\rightarrow \rightarrow 1.5[CaO\cdot 2SiO_2\cdot 2H_2O]+10.5H_2+ +0.17[3CaO\cdot Fe_2O_3\cdot 6H_2O]+2.67Fe(OH)_3, \quad (11)$$

$$2Ca(OH)_2+3FeSi+18.17H_2O\rightarrow \rightarrow 2CaO\cdot SiO_2\cdot 1.17H_2O+10.5H_2+ +2[H_4SiO_4]+3Fe(OH)_3, \quad (12)$$

$Ca(OH)_2:FeSi=5:6$

$$5Ca(OH)_2+6FeSi+30.5H_2O\rightarrow \rightarrow 5CaO\cdot 6SiO_2\cdot 5.5H_2O+21H_2+6Fe(OH)_3, \quad (13)$$

$$5Ca(OH)_2+6FeSi+31.375H_2O\rightarrow \rightarrow 1.25[4CaO\cdot 3SiO_2\cdot 1.5H_2O]+21H_2+ +2.25[H_4SiO_4]+6Fe(OH)_3, \quad (14)$$

$$5Ca(OH)_2+6FeSi+27.83H_2O\rightarrow \rightarrow 0.83[6CaO\cdot 6SiO_2\cdot H_2O]+21H_2+ +H_4SiO_4+6Fe(OH)_3, \quad (15)$$

$$5Ca(OH)_2+6FeSi+31H_2O\rightarrow \rightarrow 2[2CaO\cdot 3SiO_2\cdot 2.5H_2O]+21H_2+ +0.33[3CaO\cdot Fe_2O_3\cdot 6H_2O]+5.33Fe(OH)_3, \quad (16)$$

$$5Ca(OH)_2+6FeSi+33H_2O\rightarrow \rightarrow 3[CaO\cdot 2SiO_2\cdot 2H_2O]+21H_2+ +0.67[3CaO\cdot Fe_2O_3\cdot 6H_2O]+4.67Fe(OH)_3, \quad (17)$$

$$5Ca(OH)_2+6FeSi+34.925H_2O\rightarrow \rightarrow 2.5[2CaO\cdot SiO_2\cdot 1.17H_2O]+21H_2+ +3.5[H_4SiO_4]+6Fe(OH)_3, \quad (18)$$

$Ca(OH)_2:FeSi=6:6$

$$6Ca(OH)_2+6FeSi+30.5H_2O\rightarrow \rightarrow 5CaO\cdot 6SiO_2\cdot 5.5H_2O+21H_2+ +0.33[3CaO\cdot Fe_2O_3\cdot 6H_2O]+5.33Fe(OH)_3, \quad (19)$$

$$6Ca(OH)_2+6FeSi+29.25H_2O\rightarrow \rightarrow 1.5[4CaO\cdot 3SiO_2\cdot 1.5H_2O]+21H_2+ +1.5[H_4SiO_4]+6Fe(OH)_3, \quad (20)$$

$$6Ca(OH)_2+6FeSi+25H_2O\rightarrow \rightarrow 6CaO\cdot 6SiO_2\cdot H_2O+21H_2+6Fe(OH)_3, \quad (21)$$

$$6Ca(OH)_2+6FeSi+31H_2O\rightarrow \rightarrow 2[2CaO\cdot 3SiO_2\cdot 2.5H_2O]+21H_2+ +0.67[3CaO\cdot Fe_2O_3\cdot 6H_2O]+4.67Fe(OH)_3, \quad (22)$$

$$6Ca(OH)_2+6FeSi+33H_2O\rightarrow \rightarrow 3[CaO\cdot 2SiO_2\cdot 2H_2O]+21H_2+ +3CaO\cdot Fe_2O_3\cdot 6H_2O+4Fe(OH)_3, \quad (23)$$

$$6Ca(OH)_2+6FeSi+33.51H_2O\rightarrow \rightarrow 3[2CaO\cdot SiO_2\cdot 1.17H_2O]+21H_2+ +3[H_4SiO_4]+6Fe(OH)_3, \quad (24)$$

$Ca(OH)_2:FeSi=4:3$

$$4Ca(OH)_2+3FeSi+15.25H_2O\rightarrow \rightarrow 0.5[5CaO\cdot 6SiO_2\cdot 5.5H_2O]+10.5H_2+ +0.5[3CaO\cdot Fe_2O_3\cdot 6H_2O]+2Fe(OH)_3, \quad (25)$$

$$4Ca(OH)_2+3FeSi+12.5H_2O\rightarrow \rightarrow 4CaO\cdot 3SiO_2\cdot 1.5H_2O+10.5H_2+3Fe(OH)_3, \quad (26)$$

$$4Ca(OH)_2+3FeSi+12.5H_2O\rightarrow \rightarrow 0.5[6CaO\cdot 6SiO_2\cdot H_2O]+10.5H_2+ +0.33[3CaO\cdot Fe_2O_3\cdot 6H_2O]+2.33Fe(OH)_3, \quad (27)$$

$$4Ca(OH)_2+3FeSi+15.5H_2O\rightarrow \rightarrow 2CaO\cdot 3SiO_2\cdot 2.5H_2O+10.5H_2+ +0.67[3CaO\cdot Fe_2O_3\cdot 6H_2O]+1.67Fe(OH)_3, \quad (28)$$

$$4Ca(OH)_2+3FeSi+16.5H_2O\rightarrow \rightarrow 1.5[CaO\cdot 2SiO_2\cdot 2H_2O]+10.5H_2+ +0.83[3CaO\cdot Fe_2O_3\cdot 6H_2O]+1.33Fe(OH), \quad (29)$$

$$4Ca(OH)_2+3FeSi+15.34H_2O\rightarrow \rightarrow 2[2CaO\cdot SiO_2\cdot 1.17H_2O]+10.5H_2+ +H_4SiO_4+3Fe(OH)_3, \quad (30)$$

$Ca(OH)_2:FeSi=2:1$

$$2Ca(OH)_2+FeSi+5.17H_2O\rightarrow \rightarrow 0.17[5CaO\cdot 6SiO_2\cdot 5.5H_2O]+3.5H_2+ +0.39[3CaO\cdot Fe_2O_3\cdot 6H_2O]+0.22Fe(OH)_3, \quad (31)$$

$$2Ca(OH)_2+FeSi+4.17H_2O\rightarrow \rightarrow 0.33[4CaO\cdot 3SiO_2\cdot 1.5H_2O]+3.5H_2+ +0.22[3CaO\cdot Fe_2O_3\cdot 6H_2O]+0.56Fe(OH)_3, \quad (32)$$

$$2Ca(OH)_2+FeSi+4.17H_2O\rightarrow$$

$$\rightarrow 0.17[6CaO\cdot 6SiO_2\cdot H_2O]+3.5H_2+ +0.33[3CaO\cdot Fe_2O_3\cdot 6H_2O]+0.33Fe(OH)_3, \quad (33)$$

$$2Ca(OH)_2+FeSi+5.17H_2O\rightarrow \rightarrow 0.33[2CaO\cdot 3SiO_2\cdot 2.5H_2O]+3.5H_2+ +0.44[3CaO\cdot Fe_2O_3\cdot 6H_2O]+0.11Fe(OH)_3, \quad (34)$$

$$2Ca(OH)_2+FeSi+5.5H_2O\rightarrow \rightarrow 0.5[CaO\cdot 2SiO_2\cdot 2H_2O]+3.5H_2+ +0.5[3CaO\cdot Fe_2O_3\cdot 6H_2O], \quad (35)$$

$$2Ca(OH)_2+FeSi+4.17H_2O\rightarrow \rightarrow 2CaO\cdot SiO_2\cdot 1.17H_2O+3.5H_2+Fe(OH)_3. \quad (36)$$

For the $FeSi_2-Ca(OH)_2-H_2O$ system, the following reactions with a similar ratio of calcium hydroxide to the ferrosilicon were considered:

$Ca(OH)_2:FeSi_2=1:2$

$$Ca(OH)_2+FeSi_2+8.7H_2O\rightarrow \rightarrow 0.2[5CaO\cdot 6SiO_2\cdot 5.5H_2O]+5.5H_2+ +0.8[H_4SiO_4]+Fe(OH)_3, \quad (37)$$

$$Ca(OH)_2+FeSi_2+8.875H_2O\rightarrow \rightarrow 0.25[4CaO\cdot 3SiO_2\cdot 1.5H_2O]+5.5H_2+ +1.25[H_4SiO_4]+Fe(OH)_3, \quad (38)$$

$$Ca(OH)_2+FeSi_2+8.23H_2O\rightarrow \rightarrow 0.17[6CaO\cdot 6SiO_2\cdot H_2O]+5.56H_2+ +H_4SiO_4+Fe(OH)_3, \quad (39)$$

$$Ca(OH)_2+FeSi_2+8.25H_2O\rightarrow \rightarrow 0.5[2CaO\cdot 3SiO_2\cdot 2.5H_2O]+5.5H_2+ +0.5[H_4SiO_4]+Fe(OH)_3, \quad (40)$$

$$Ca(OH)_2+FeSi_2+8H_2O\rightarrow \rightarrow CaO\cdot 2SiO_2\cdot 2H_2O+5.5H_2+Fe(OH)_3, \quad (41)$$

$$Ca(OH)_2+FeSi_2+9.585H_2O\rightarrow \rightarrow 0.5[2CaO\cdot SiO_2\cdot 1.17H_2O]+5.5H_2+ +1.5[H_4SiO_4]+Fe(OH)_3, \quad (42)$$

$Ca(OH)_2:FeSi_2=2:3$

$$2Ca(OH)_2+1.5FeSi_2+11.9H_2O\rightarrow \rightarrow 0.4[5CaO\cdot 6SiO_2\cdot 5.5H_2O]+8.25H_2+ +0.6[H_4SiO_4]+1.5Fe(OH)_3, \quad (43)$$

$$2Ca(OH)_2+1.5FeSi_2+12.25H_2O\rightarrow \rightarrow 0.5[4CaO\cdot 3SiO_2\cdot 1.5H_2O]+8.25H_2+ +1.5[H_4SiO_4]+1.5Fe(OH)_3, \quad (44)$$

$$2Ca(OH)_2+1.5FeSi_2+10.83H_2O\rightarrow \rightarrow 0.33[6CaO\cdot 6SiO_2\cdot H_2O]+8.25H_2+ +H_4SiO_4+1.5Fe(OH)_3, \quad (45)$$

$$2Ca(OH)_2+1.5FeSi_2+11H_2O\rightarrow \rightarrow 2CaO\cdot 3SiO_2\cdot 2.5H_2O+8.25H_2+1.5Fe(OH)_3, \quad (46)$$

$$2Ca(OH)_2+1.5FeSi_2+13.5H_2O\rightarrow \rightarrow CaO\cdot 2SiO_2\cdot 2H_2O+8.25H_2+H_4SiO_4+ 0.33[3CaO\cdot Fe_2O_3\cdot 6H_2O]+0.83Fe(OH)_3, \quad (47)$$

$$2Ca(OH)_2+1.5FeSi_2+13.67H_2O\rightarrow \rightarrow 2CaO\cdot SiO_2\cdot 1.17H_2O+8.25H_2+ +2[H_4SiO_4]+1.5Fe(OH)_3, \quad (48)$$

$Ca(OH)_2:FeSi_2=5:6$

$5Ca(OH)_2+3FeSi_2+21.5H_2O\rightarrow$
$\rightarrow 5CaO\cdot 6SiO_2\cdot 5.5H_2O+16.5H_2+3Fe(OH)_3$, (49)

$5Ca(OH)_2+3FeSi_2+22.375H_2O\rightarrow$
$\rightarrow 1.25[4CaO\cdot 3SiO_2\cdot 1.5H_2O]+16.5H_2+$
$+2.25[H_4SiO_4]+3Fe(OH)_3$, (50)

$5Ca(OH)_2+3FeSi_2+18.83H_2O\rightarrow$
$\rightarrow 0.83[6CaO\cdot 6SiO_2\cdot H_2O]+16.5H_2+$
$+H_4SiO_4+3Fe(OH)_3$, (51)

$5Ca(OH)_2+3FeSi_2+22H_2O\rightarrow$
$\rightarrow 2[2CaO\cdot 3SiO_2\cdot 2.5H_2O]+16.5H_2+$
$+0.33[3CaO\cdot Fe_2O_3\cdot 6H_2O]+2.33Fe(OH)_3$, (52)

$5Ca(OH)_2+3FeSi_2+24H_2O\rightarrow$
$\rightarrow 3[CaO\cdot 2SiO_2\cdot 2H_2O]+16.5H_2+$
$+0.67[3CaO\cdot Fe_2O_3\cdot 6H_2O]+1.67Fe(OH)_3$, (53)

$5Ca(OH)_2+3FeSi_2+25.925H_2O\rightarrow$
$\rightarrow 2.5[2CaO\cdot SiO_2\cdot 1.17H_2O]+16.5H_2+$
$+3.5[H_4SiO_4]+3Fe(OH)_3$, (54)

$Ca(OH)_2:FeSi_2=6:6$

$6Ca(OH)_2+3FeSi_2+21.5H_2O\rightarrow$
$\rightarrow 5CaO\cdot 6SiO_2\cdot 5.5H_2O+16.5H_2+$
$+0.33[3CaO\cdot Fe_2O_3\cdot 6H_2O]+2.33Fe(OH)_3$, (55)

$6Ca(OH)_2+3FeSi_2+20.25H_2O\rightarrow$
$\rightarrow 1.5[4CaO\cdot 3SiO_2\cdot 1.5H_2O]+16.5H_2+$
$+1.5[H_4SiO_4]+3Fe(OH)_3$, (56)

$6Ca(OH)_2+3FeSi_2+16H_2O\rightarrow$
$\rightarrow 6CaO\cdot 6SiO_2\cdot H_2O+16.5H_2+3Fe(OH)_3$, (57)

$6Ca(OH)_2+3FeSi_2+22H_2O\rightarrow$
$\rightarrow 2[2CaO\cdot 3SiO_2\cdot 2.5H_2O]+16.5H_2+$
$+0.67[3CaO\cdot Fe_2O_3\cdot 6H_2O]+1.67Fe(OH)$, (58)

$6Ca(OH)_2+3FeSi_2+24H_2O\rightarrow$
$\rightarrow 3[CaO\cdot 2SiO_2\cdot 2H_2O]+16.5H_2+$
$+3CaO\cdot Fe_2O_3\cdot 6H_2O+Fe(OH)_3$, (59)

$6Ca(OH)_2+3FeSi_2+24.51H_2O\rightarrow$
$\rightarrow 3[2CaO\cdot SiO_2\cdot 1.17H_2O]+16.5H_2+$
$+3[H_4SiO_4]+3Fe(OH)_3$, (60)

$Ca(OH)_2:FeSi_2=4:3$

$4Ca(OH)_2+1.5FeSi_2+10.75H_2O\rightarrow$
$\rightarrow 0.5[5CaO\cdot 6SiO_2\cdot 5.5H_2O]+8.25H_2+$
$+0.5[3CaO\cdot Fe_2O_3\cdot 6H_2O]+0.5Fe(OH)_3$, (61)

$4Ca(OH)_2+1.5FeSi_2+8H_2O\rightarrow$
$\rightarrow 4CaO\cdot 3SiO_2\cdot 1.5H_2O+8.25H_2+1.5Fe(OH)_3$, (62)

$4Ca(OH)_2+1.5FeSi_2+8H_2O\rightarrow$
$\rightarrow 0.5[6CaO\cdot 6SiO_2\cdot H_2O]+8.25H_2+$
$+0.33[3CaO\cdot Fe_2O_3\cdot 6H_2O]+0.83Fe(OH)_3$, (63)

$4Ca(OH)_2+1.5FeSi_2+11H_2O\rightarrow$
$\rightarrow 2CaO\cdot 3SiO_2\cdot 2.5H_2O+8.25H_2+$
$+0.67[3CaO\cdot Fe_2O_3\cdot 6H_2O]+0.17Fe(OH)_3$, (64)

$4Ca(OH)_2+1.5FeSi_2+11.5H_2O\rightarrow$
$\rightarrow 1.5[CaO\cdot 2SiO_2\cdot 2H_2O]+8H_2+$
$+0.75[3CaO\cdot Fe_2O_3\cdot 6H_2O]$, (65)

$4Ca(OH)_2+1.5FeSi_2+10.84H_2O\rightarrow$
$\rightarrow 2[2CaO\cdot SiO_2\cdot 1.17H_2O]+8.25H_2+$
$+H_4SiO_4+1.5Fe(OH)_3$, (66)

$Ca(OH)_2:FeSi_2=2:1$

$2Ca(OH)_2+0.5FeSi_2+3.58H_2O\rightarrow$
$\rightarrow 0.17[5CaO\cdot 6SiO_2\cdot 5.5H_2O]+2.75H_2+$
$+0.25[3CaO\cdot Fe_2O_3\cdot 6H_2O]+0.42Ca(OH)_2$, (67)

$2Ca(OH)_2+0.5FeSi_2+2.67H_2O\rightarrow$
$\rightarrow 0.33[4CaO\cdot 3SiO_2\cdot 1.5H_2O]+2.75H_2+$
$+0.22[3CaO\cdot Fe_2O_3\cdot 6H_2O]+0.06Fe(OH)_3$, (68)

$2Ca(OH)_2+0.5FeSi_2+2.67H_2O\rightarrow$
$\rightarrow 0.17[6CaO\cdot 6SiO_2\cdot H_2O]+2.75H_2+$
$+0.25[3CaO\cdot Fe_2O_3\cdot 6H_2O]+0.25Ca(OH)_2$, (69)

$2Ca(OH)_2+0.5FeSi_2+3.67H_2O\rightarrow$
$\rightarrow 0.33[2CaO\cdot 3SiO_2\cdot 2.5H_2O]+2.75H_2+$
$+0.25[3CaO\cdot Fe_2O_3\cdot 6H_2O]+0.58Fe(OH)_3$, (70)

$2Ca(OH)_2+0.5FeSi_2+4H_2O\rightarrow$
$\rightarrow 0.5[CaO\cdot 2SiO_2\cdot 2H_2O]+2.75H_2+$
$+0.25[3CaO\cdot Fe_2O_3\cdot 6H_2O]+0.75Ca(OH)$, (71)

$2Ca(OH)_2+0.5FeSi_2+2.67H_2O\rightarrow$
$\rightarrow 2CaO\cdot SiO_2\cdot 1.17H_2O+2.75H_2+0.5Fe(OH)_3$. (72)

The analysis of the results of the performed calculations (Tables 1 and 2) shows that the lowest value of the Gibbs energy change for the formation of hydrosilicates corresponds to the stoichiometric ratios of the initial components (reactions (5), (10), (13), (21), (26), (36), (41), (46), (49), (57), (62), and (72)).

The temperature dependences of the change in Gibbs energy are ambiguous and depend on the ratio of calcium hydroxide to ferrosilicon in the hydrated system (Figs. 1 and 2). Thus, for the ratio of reagents of 1:2, gyrolite is thermodynamically more stable up to 420 K. However, okenite becomes more stable at a further increase in temperature (Fig. 1,a, reactions (4) and (5)). At the ratios $Ca(OH)_2$:FeSi=2:1 and 6:6, hillebrandite is thermodynamically more stable than all other calcium hydrosilicates with increasing temperature (Fig. 1,f, reaction (36)).

The analysis of the results obtained for the $FeSi_2$–$Ca(OH)_2$–H_2O system shows that xonotlite is more thermodynamically stable for the ratio $Ca(OH)_2$:$FeSi_2$=6:6 up to 360 K. Gyrolite becomes more stable at temperatures higher than 360 K (Fig. 2,d, reactions (57) and (58)). Thus, gyrolite and foshagite are thermodynamically stable with increasing temperature for the ratio $Ca(OH)_2$:$FeSi_2$=4:3, and when the temperature reaches 330 K, gyrolite is found to be more stable (Fig. 2,e, reactions (62) and (64)).

Conclusions

The performed thermodynamic study showed the possibility of directed synthesis of the mineralogical composition of hydration products in the $Ca(OH)_2$–FeSi (or $FeSi_2$)–H_2O systems. The presented theoretical results clear up the mechanisms of hydration of the astringents and building materials on their basis. The obtained data can be used to study physicochemical processes occurring in aerated concretes, which are hardened by both autoclave

Table 1

The values of Gibbs energy for the reactions of hydrosilicate formation at different basicity in the $Ca(OH)_2$:FeSi system

No.	Product of reaction	$-\Delta G^0_{298}$, kJ/mol					
		$Ca(OH)_2$:FeSi					
		1/2	2/3	5/6	6/6	4/3	2/1
1	Tobermorite $5CaO\cdot6SiO_2\cdot5.5H_2O$	685.411	1070.045	2223.944	2237.223	1156.065	409.807
2	Foshagite $4CaO\cdot3SiO_2\cdot1.5H_2O$	666.533	1032.287	2129.550	2194.527	1162.240	381.441
3	Xonotlite $6CaO\cdot6SiO_2\cdot H_2O$	676.162	1014.681	2131.615	2341.559	1144.957	416.311
4	Gyrolite $2CaO\cdot3SiO_2\cdot2.5H_2O$	694.739	1088.700	2190.678	2236.190	1147.491	367.055
5	Okenite $CaO\cdot2SiO_2\cdot2H_2O$	700.546	1081.634	2176.547	2189.826	1108.192	394.367
6	Hillebrandite $2CaO\cdot SiO_2\cdot1.17H_2O$	655.675	1010.572	2075.263	2129.382	1118.810	421.757

Table 2

The values of Gibbs energy for the reactions of hydrosilicate formation at different basicity in the $Ca(OH)_2$:$FeSi_2$ system

No.	Product of reaction	$-\Delta G^0_{298}$, kJ/mol					
		$Ca(OH)_2$:$FeSi_2$					
		1/2	2/3	5/6	6/6	4/3	2/1
1	Tobermorite $5CaO\cdot6SiO_2\cdot5.5H_2O$	755.931	1175.824	2435.504	2448.783	1261.845	444.276
2	Foshagite $4CaO\cdot3SiO_2\cdot1.5H_2O$	737.052	1138.067	2341.110	2406.086	1269.387	416.701
3	Xonotlite $6CaO\cdot6SiO_2\cdot H_2O$	760.349	1120.461	2343.175	2463.866	1235.993	467.681
4	Gyrolite $2CaO\cdot3SiO_2\cdot2.5H_2O$	765.259	1194.479	2402.238	2445.429	1268.019	312.635
5	Okenite $CaO\cdot2SiO_2\cdot2H_2O$	771.066	1120.383	2388.106	2401.385	1123.379	429.607
6	Hillebrandite $2CaO\cdot SiO_2\cdot1.17H_2O$	726.195	1116.352	2286.823	2340.942	1224.590	476.916

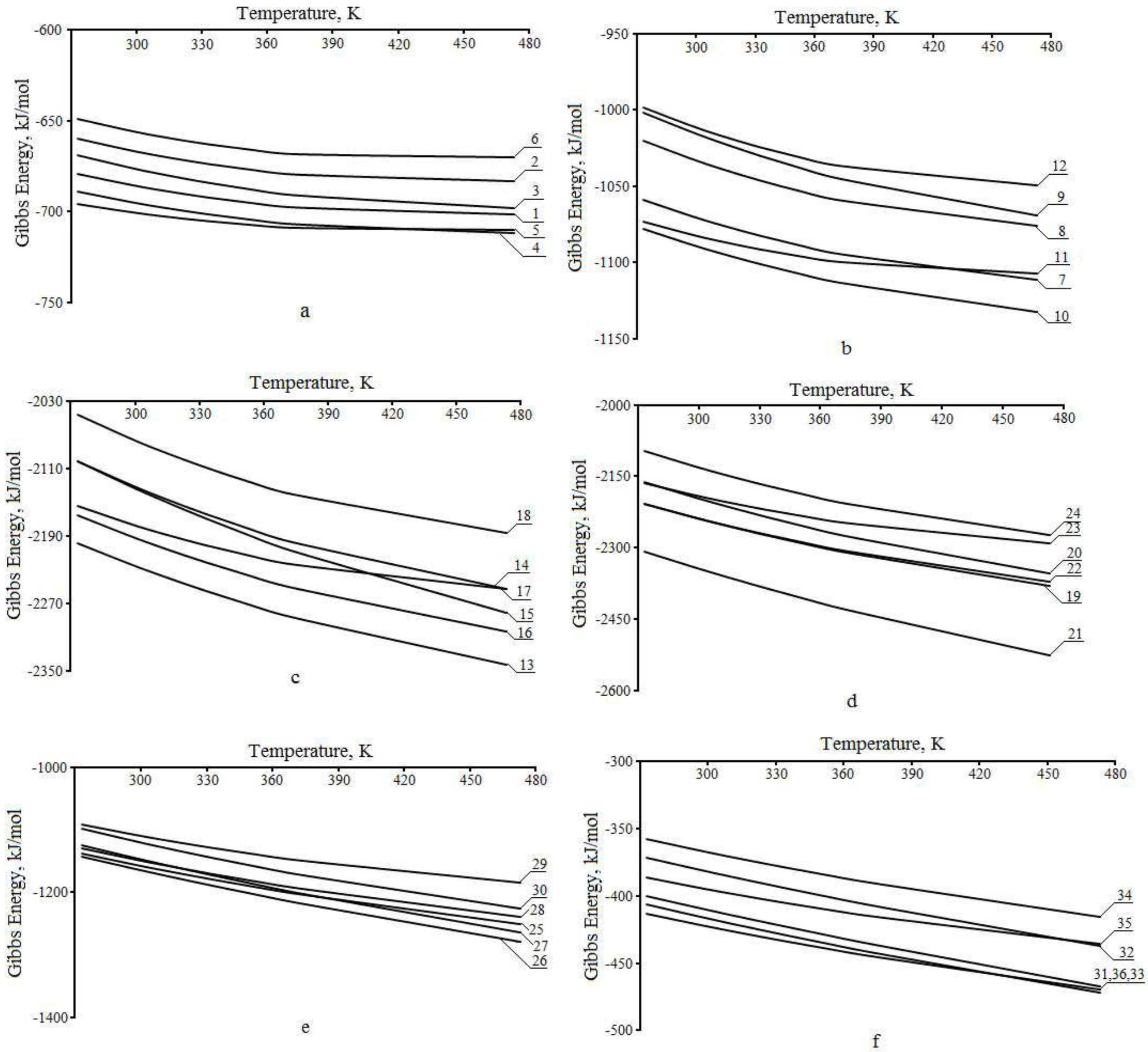

Fig. 1. Temperature dependences of Gibbs energy at different ratio $Ca(OH)_2$:FeSi:
a – 1:2; b – 2:3; c – 5:6; d – 6:6; e – 4:3; f – 2:1

and non-autoclave methods and contain ferrosilicon of different chemical compositions as a gasifier.

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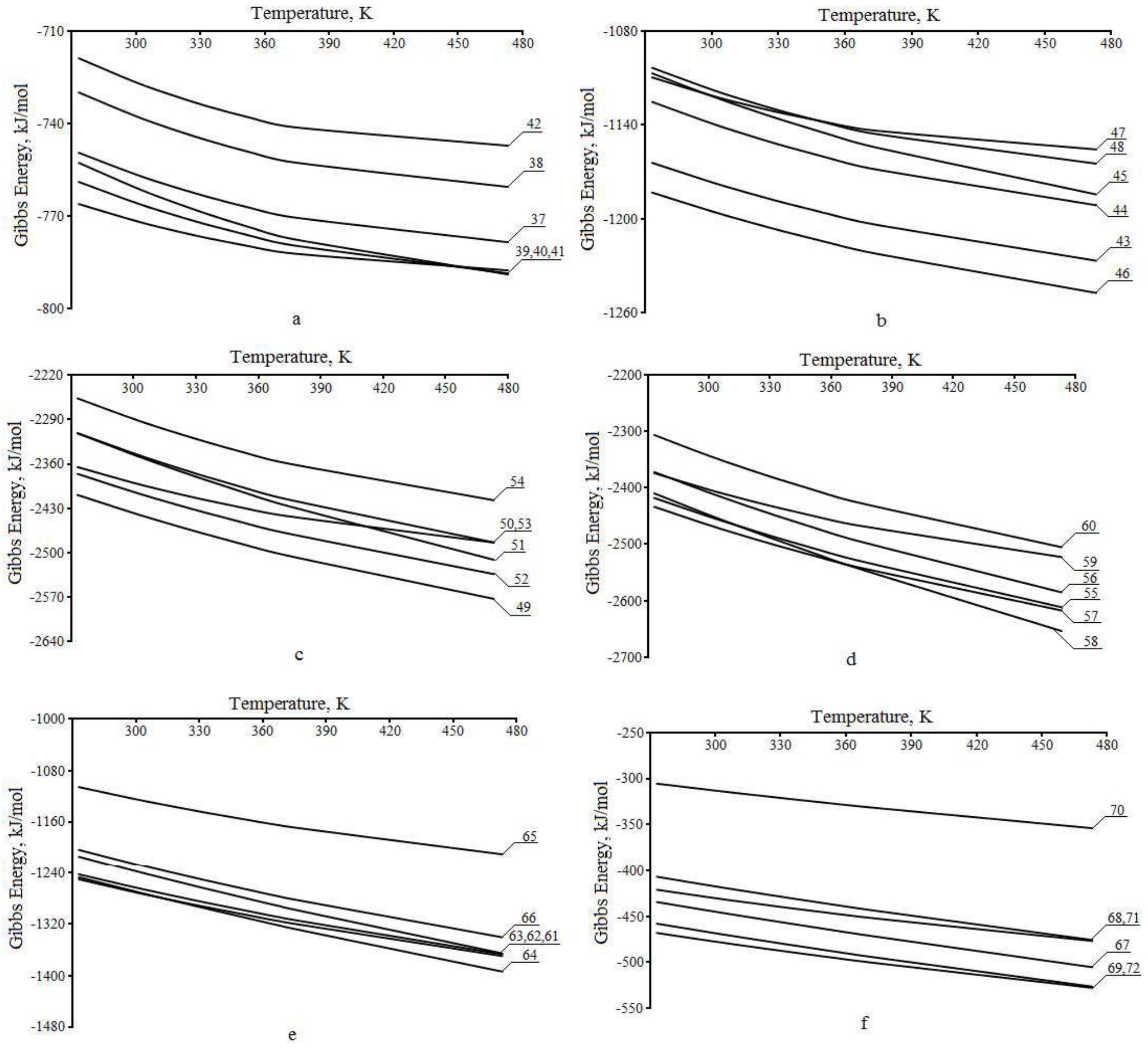

Fig. 2. Temperature dependences of Gibbs energy at different ratio $Ca(OH)_2$:$FeSi_2$:
a – 1:2; b – 2:3; c – 5:6; d – 6:6; e – 4:3; f – 2:1

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ТЕРМОДИНАМІЧНИЙ АНАЛІЗ ХІМІЧНИХ РЕАКЦІЙ В СИСТЕМАХ $FeSi-Ca(OH)_2-H_2O$ І $FeSi_2-Ca(OH)_2-H_2O$

А.О. Мусіна, О.О. Сігунов, Т.В. Кравченко, А.О. Гура

Використання термодинамічного аналізу в технології силікатів є невід'ємною частиною наукових досліджень і важливою складовою при вивченні процесів гідратації. Термодинамічний аналіз дозволяє обґрунтувати напрямок, за яким відбуваються процеси гідратації мінеральних в'яжучих, а також стійкість гідратних утворень, які визначають міцність бетонів. Для дослідження процесів тверднення необхідно розглянути термодинаміку реальних розчинів в'яжучих у воді та термодинаміку співіснування змішаних кристалічних фаз. Нами виконано термодинамічний аналіз реакцій гідратації в системах $FeSi-Ca(OH)_2-H_2O$ та $FeSi_2-Ca(OH)_2-H_2O$, які характерні для технології виробництва ніздрюватих газобетонів. В досліджуваній системі показана можливість виконувати направлений синтез мінералогічного складу продуктів гідратації. Встановлено послідовність хімічних реакцій і залежність їх протікання від температури. Надані теоретичні дослідження розширюють уявлення про механізми гідратації в'яжучих і будівельних матеріалів на їх основі, зокрема при вивченні фізико-хімічних процесів, що перебігають в газобетонах автоклавного і неавтоклавного тверднення, які містять в якості газоутворювача феросиліцій різного хімічного складу.

Ключові слова: газобетон, феросиліцій, термодинамічний аналіз, вапно, гідратація, мінералоутворення, енергія Гіббса.

THERMODYNAMIC ANALYSIS OF CHEMICAL REACTIONS IN THE SYSTEMS $FeSi-Ca(OH)_2-H_2O$ AND $FeSi_2-Ca(OH)_2-H_2O$

*A.O. Musina, O.O. Sihunov *, T.V. Kravchenko, A.O. Hura*

Ukrainian State University of Chemical Technology, Dnipro, Ukraine

*** e-mail: alsigunov@ukr.net**

The use of thermodynamic analysis in silicate technology is an integral part of scientific research and an important component in the study of hydration processes. Thermodynamic analysis allowed substantiating the path of the processes of mineral binders hydration and the stability of hydrated formations, which affects the strength of the concrete. To investigate the solidification processes, one should consider both the thermodynamics of the real solutions of astringent in water and the thermodynamics of the coexistence of mixed crystalline phases. We carried out the thermodynamic analysis of hydration reactions in the systems $FeSi-Ca(OH)_2-H_2O$ and $FeSi_2-Ca(OH)_2-H_2O$, that are used in the production of cellular gas concretes. We showed that there is a possibility to perform directed synthesis of the mineralogical composition of hydration products in the systems under study. The sequence of the chemical reactions and their temperature dependences are established. The developed theoretical model allows understanding the mechanisms of hydration of astringent and building materials on their basis, in particular in the study of physicochemical processes occurring in aerated concretes, prepared by both autoclave and non-autoclave curing, which contain gas-forming ferrosilicon of different chemical compositions.

Keywords: aerated concrete; ferrosilicon; thermodynamic analysis; lime; hydration; mineral formation; Gibbs energy.

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