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Research article

Thermodynamic and kinetic study of CaS in aqueous systems

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A B S T R A C T

One of the main sources of sulfide in fuel combustion ashes is the hazardous compound calcium sulfide (CaS), which decomposes in water and releases sulfide compounds into the environment. In order to safely use hydrotransport and open air deposition of wet ash, as well as to treat alkaline ash transportation waters, it is important to know the dissolution behavior of CaS, in this regard, several values of both CaS solubility and equilibrium constants of dissolution reactions are illustrated in the scientific literature. To reconcile these differences, both kinetics and equilibrium of CaS dissolution reactions under inert and air conditions at 25 °C were studied. The water solubility of CaS under an inert atmosphere (with N_2 treated water) is lower ($2.29 \cdot 10^{-3}$ mol/L) than under air ($2.74 \cdot 10^{-3}$ mol/L). A more complex reaction mechanism for open air dissolution, elucidated using HsC Chemistry® 7.1 simulations, was also presented. Various reaction mechanisms as well as equilibrium and rate constants were evaluated to model CaS dissolution data. The relatively small deviations between calculated values and experimental data confirm that the suggested models could be employed to describe CaS dissolution under both atmospheric and inert conditions.

1. Introduction

With regard to atmospheric emissions (e.g. CO_2, SO_2), the most serious problem caused by the extensive use of oil shale is the safe disposal of the related mineral waste (8.0 MT in 2013) [1]. The sulfur content (<2% in Estonian oil shale) in oil shale power plant ash depends on the combustion technology and operating parameters such as boiler temperature and pressure as well as the presence of reductive and oxidative zones. More sulfur is bound into power plant ash as $CaSO_4$ using circulating fluidized bed (CFB) technology (up to 10.9 wt.%) compared with pulverized firing (PF) technology (up to 5.4 wt.%). CaS concentrations values are typically <0.2 wt.%; however concentration values up to 0.7 wt.% can be found in CFB ash [2,3,4] and almost up to 3 wt.% is found in the solid waste from shale oil production [5,6]. CaS is the most hazardous sulfur based compound for the environment [7,8], it forms during both ash sulfation and fuel combustion as well as thermal processing over both calcium oxide (Eqs. (1)–(2)) and carbon (Eqs. (3)–(4)) [8,9].

$$4CaO + 4SO_2 \rightleftarrows CaS + 3CaSO_4 \quad (1)$$

$$CaO + H_2S \rightleftarrows CaS + H_2O \quad (2)$$

$$CaSO_4 + 4C(char) \rightleftarrows CaS + 4CO \quad (3)$$

$$CaCO_3 + H_2S \rightleftarrows CaS + H_2O + 4CO_2 \quad (4)$$

CaS is chemically unstable in open air and also disintegrates at the ash dump site during leaching. Upon hydration, CaS decomposes releasing sulfides into the environment and generates toxic H_2S under acidic conditions [4]. To mitigate its environmental impact, one must understand the behavior of CaS in a complex mixture of leachable substances within both power plant ashes and shale oil production ash during both hydrotransport or while treating ash leachates with CO_2 containing gas to reduce its alkalinity and produce precipitated $CaCO_3$ as a commercial by-product [4,10]. Accurate thermodynamic measurements are prerequisite to this goal.

Literature information about CaS leaching is currently ambiguous. Since the dissolution mechanism is complex, different values have been given for the CaS solubility (Table 1). This study aims to resolve this discrepancy by investigating the dissolution mechanisms of CaS on the basis of both thermodynamic equilibrium and reaction kinetics. The new proposed mathematical models simulate the CaS dissolution process under various conditions and enable to both predict the dynamics of CaS leaching at ash dumping sites and optimize operating conditions to avoid H_2S emissions during the precipitation of $CaCO_3$ from oil shale ash.

More specifically, the current paper presents reaction models built for the CaS–H_2O system under both an inert and air atmosphere using experimentally determined CaS solubility data as well as reactions kinetics.

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Table 1
Values for water solubility of CaS.

Temp. (°C)	Input data	mol/L	Reference
20	0.212 g per 1 L	$2.94 \cdot 10^{-3}$	Riesenfeld and Feld (1921) [11]
Room temperature	0.02 parts per 100 parts in water; decomposing	$2.77 \cdot 10^{-3}$	Dean (1999) [12]
Room temperature	0.02 parts per 100 parts in water; decomposing	$2.77 \cdot 10^{-3}$	CRC Handbook (2006) [13]
25	1.733 mmol/L	$1.73 \cdot 10^{-3}$	Zekker et al. (2011) [14]
25	0.1 wt.%	$1.38 \cdot 10^{-2}$	Licht (1988) [15]
25	<1 g/L; decomposes	$<1.38 \cdot 10^{-2}$	Perry and Green (1999) [16]
15	0.01 g per 100 cm^3 solution	$1.39 \cdot 10^{-3}$	Linke (1958) [17]

2. CaS dissolution mechanism — generalization of literature data

2.1. CaS–H_2O system under an inert environment

CaS leaching under inert conditions corresponds to the dissolution environment in the deeper layers within ash piles. The CaS dissolution reaction, Eq. (5), and thermodynamic equilibrium constant K_1, Eq. (6), of calcium sulfide (CaS) can be defined as follows [7,14,18–19]:

$$[\mathrm{CaS}(s)] \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \left[\mathrm{Ca}^{2+}\right] + \left[\mathrm{S}^{2-}\right] \tag{5}$$

$$K_1 = \left[\mathrm{Ca}^{2+}\right] \times \left[\mathrm{S}^{2-}\right] \tag{6}$$

Mölder et al. (1995) [7] reported that the first order rate constants for CaS hydrolysis are 0.0467 and 0.0936 h^{-1} at 20 °C and 40 °C, respectively.

CaS dissolution determines with a noticeable change in the system pH due to the formation of HS^- and H_2S as S^{2-} dissociation products (Eqs. (7) and (9)). The dissociation of S^{2-} can be characterized by the basicity constants K_{b2} and K_{b1} (Eqs. (8) and (10)) [14].

$$\left[\mathrm{S}^{2-}\right] + [\mathrm{H_2O}] \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} [\mathrm{HS}^-] + [\mathrm{OH}^-] \tag{7}$$

$$K_{b2} = \frac{[\mathrm{HS}^-] \times [\mathrm{OH}^-]}{\left[\mathrm{S}^{2-}\right]} \tag{8}$$

$$[\mathrm{HS}^-] + [\mathrm{H_2O}] \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} [\mathrm{H_2S}] + [\mathrm{OH}^-] \tag{9}$$

$$K_{b1} = \frac{[\mathrm{H_2S}] \times [\mathrm{OH}^-]}{[\mathrm{HS}^-]} \tag{10}$$

Equilibrium between the phases of molecular sulfide can be given as follows [20]:

$$[\mathrm{H_2S}(aq)] \rightleftarrows [\mathrm{H_2S}(g)] \tag{11}$$

The equilibrium between the water-soluble hydrogen sulfide and gas form is set by Henry–Dalton's law as $x(g) = k_H \cdot p(g)$, where $x(g)$ — the concentration of gas in solution expressed through the mole fraction (the number of gas moles divided by the total number of moles of the solution), k_H — Henry constant, the gas mole fraction in the solution, Pa^{-1} and $p(g)$ — the partial pressure of the gas above the solution, Pa. Carroll and Mather [21] presented the proportionality coefficient (k_H) value for H_2S at 25 °C as 0.018 mol frac/MPa.

Water autoprotolysis (H_2O dissociation) must also be taken into account:

$$[\mathrm{H_2O}] \rightleftarrows [\mathrm{H}^+] + [\mathrm{OH}^-] \tag{12}$$

The ion-product constant of water, K_w is expressed as follows [14, 22]:

$$K_w = \left[\mathrm{H}^+\right] \times [\mathrm{OH}^-] = 10^{-14} \tag{13}$$

The activity coefficients in CaS water system were expected approximately equal to 1 and have therefore been excluded.

According to CaS dissolution mechanism described above, the solubility product (K_{sp}) (Eq. (14)) is calculated as a product of ions in the saturated solution from Eq. (6), using the concentrations of total sulfide $[S_{\mathrm{sulfide}} = [S^{2-}] + [HS^-] + [H_2S(aq)]]$ and calcium $[Ca^{2+}]$:

$$K_{sp} = \left[\mathrm{Ca}^{2+}\right] \times \left[\mathrm{S}^{2-}\right]_{tot} = \left[\mathrm{Ca}^{2+}\right] \times \left[\mathrm{Ca}^{2+}\right] \tag{14}$$

Since the solution contains equal amount of calcium and sulfide ions, the value of K_1 can be expressed as the square of Ca-ion content.

The dissolution of CaS can also be described by hydrolysis, excluding S^{2-} formation [7] (Eq. (15)), and the reaction equilibrium can be calculated as the ion-product K_s, Eq. (16):

$$[\mathrm{CaS}] + [\mathrm{H_2O}] \rightleftarrows \left[\mathrm{Ca}^{2+}\right] + [\mathrm{HS}^-] + [\mathrm{OH}^-] \tag{15}$$

$$K_S = \left[\mathrm{Ca}^{2+}\right] \times [\mathrm{HS}^-] \times [\mathrm{OH}^-] \tag{16}$$

As a quotient of K_s to the second basicity constant (K_{b2}) [14], which simplifies to Eq. (6):

$$K_s / K_{b2} = \left[\mathrm{Ca}^{2+}\right] \times \left[\mathrm{S}^{2-}\right] = K_1 \tag{17}$$

The above equation is used in the current study for describing the dissociation equilibrium of CaS.

2.2. CaS–H_2O system under an oxidizing environment

Although the oxidation of sulfides has been extensively studied [7, 19,20,23–25], uncertainties regarding oxidation rates, mechanisms, and formation of products still remain. Several processes have been proposed for sulfide oxidation in aqueous systems. Both the reaction mechanism and the nature of the products strongly depend on the water system pH [7,25–28]. The formation of sulfur and polysulfides is unlikely under alkaline conditions ($pH > 9$) [29] and when the sulfur-oxygen ratio is small [25]. The following simplified chain of oxidation reactions was proposed for deeply alkaline systems by Mölder et al. (1995) [7], where HS^- is the main reacting sulfide species and the most stable reduced sulfide oxidation forms are thiosulfate (Eq. (18)) and sulfate (Eq. (19)):

$$2\mathrm{HS}^- + 2\mathrm{O}_2 \xrightarrow{k_4} \mathrm{S_2O_3^{2-}} + \mathrm{H_2O} \tag{18}$$

$$\mathrm{HS}^- + 2\mathrm{O}_2 \xrightarrow{k_5} \mathrm{SO_4^{2-}} + \mathrm{H}^+ \tag{19}$$

It was assumed that reactions (18) and (19) display first order kinetics and proceed simultaneously. Mölder et al. (1995) [7] investigated