

# MODEL OF THE SYSTEM OF CALCIUM SULPHATE, CALCIUM SULPHIDE AND WATER

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## ABSTRACT

Calcium sulphide and calcium sulphate are permanent components in the solid and liquid waste of oil shale industry in North East of Estonia due to the limestone containing basement. Solid calcium sulphide in contact with water according to the solubility product value will add to the liquid phase sulphide anions, which reacting with water are forming  $\text{HS}^-$  and  $\text{H}_2\text{S}$ . Hydroxide ions formed at the same processes will change the pH value of water.

In present paper the model is presented for describing the equilibrium state of the given system. For calculation of concentrations of seven different particles present in the liquid phase ( $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{S}^{2-}$ ,  $\text{HS}^-$ ,  $\text{H}_2\text{S}$ ,  $\text{OH}^-$  and  $\text{H}_3\text{O}^+$ ) seven equations are composed. Concentrations of  $\text{SO}_4^{2-}$  and  $\text{S}^{2-}$  ions in liquid phase at the equilibrium state are negligible and were not taken into account when solving composed equations. Despite of low values of concentrations of both ions in the liquid phase they are influencing the equilibrium state of the system.

First and second step dissociation constants of  $\text{H}_2\text{S}$  (accordingly presented as  $K_{a1}$  and  $K_{a2}$ ) from literature were used for mathematical solution of equations. It was found that  $\text{p}K_{a1}$  value for the first step of ionization of  $\text{H}_2\text{S}$  in water at  $25^\circ\text{C}$  is 7.01 having low deviation rate of the values published by different authors. The value of  $\text{p}K_{a2}$  for second step of ionization of  $\text{H}_2\text{S}$ , is scattering in wide range, from  $13.1 \div 17.1$  (at  $t = 20^\circ\text{C}$ ) and from  $13.78 \div 15.19$  (at  $t = 25^\circ\text{C}$ ). Calculated concentrations of the components in equilibrium state of the system are significantly depending on the  $\text{p}K_{a2}$  value. Using developed model and average values of  $\text{p}K_{a1} = 7.01$  and  $\text{p}K_{a2} = 14.63$  at  $t = 25^\circ\text{C}$ , the calculated pH value was estimated 12.5. The proposed model is useful for modeling systems containing  $\text{CaS}$  and  $\text{CaSO}_4$ , which are quite common in polluted areas with limestone basement.