

Transformations of sulfur compounds in oil shale ash suspension

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Abstract

Oil shale (sulfur content <2%) is mainly used for the production of electricity and heat in Estonia. Calcium-rich waste formed in the process of oil shale combustion can be used as sorbents in the CO₂ mineralisation process. CaSO₄ is the main sulfur compound in the ashes of oil shale, but traces of sulfides are also found. This means that transformations of sulfur compounds in the water environment must be considered while using hydrotransport and open air deposition of oil shale ash as well as treating alkaline ash transportation waters. The transformations of sulfur compounds in model systems (ash – water and CaS – water) were studied in anaerobic and aerobic conditions as well as in the process of aqueous carbonization. The separation of poisonous H₂S(g) was continuously monitored. The results revealed that the leachates of oil shale ash contained mainly sulfates in both aerobic and anaerobic conditions but sulfides and sulfites were also present. Small amount of H₂S(g) was emitted already in the first minutes of carbonation process at high pH region (~12). The alkalinity decreased during carbonation of ash – water suspensions, triggering substantial H₂S release at pH<9 (the content of H₂S(g) in off-gas reached to 110 ppm). Taking environmental issues into consideration, the critical pH value of the aqueous carbonation system of oil shale ash must be optimized in order to minimize the separation of gaseous H₂S emissions.

Keywords: calcium sulfide, oil shale ash, mineral carbonisation, H₂S.

1 Introduction

Considering the importance of energetic safety, a local low-calorific fossil fuel oil shale (sulfur content 1–2%), is used for heat power production in the



Republic of Estonia. The oil shale-fired power plants use pulverized firing (PF) as well as circulating fluidized bed combustion (FBC) technologies. The main contaminants are SO_x , NO_x , particulate matter and CO_2 . PF is related to relatively high SO_2 emissions (concentration of SO_2 in flue gases is $\sim 2200 \text{ mg/nm}^3$) [1]. The majority of sulfur emissions pass over the sea, where they deposit as acid and mix with the water upper layers, decreasing the pH of seawater. The lower part of the sulfur emissions falls on continental soils and fresh waters downwind [2]. FBC eliminates SO_2 emissions almost completely; the latter is bound into solid mineral waste – oil shale ash (OSA) [3]. Most of the OSA is deposited in waste piles due to current lack of practical applications and becomes the source of solid, liquid and gaseous pollutants. Various studies have shown that leaching of the minerals and organics from OSA-s is a continuous and relatively long-term process, which means that the ash piles contaminate the environment for a long time [4–6]. CaSO_4 is the main sulfur compound present in the oil shale ashes, but also traces of sulfides are found [7, 8]. Series of reactions (eqns. (1)–(6)), [5, 8, 9]) occur during ash contact with water and atmospheric components at open-air deposits, including release of gaseous hydrogen sulfide ($\text{H}_2\text{S}(\text{g})$) [3, 9] under certain conditions. $\text{H}_2\text{S}(\text{g})$ is an extremely toxic and irritating gas, which affects the nervous system, intermits breathing or impairs cardiac function. People can smell H_2S at low concentrations 0.0005–0.3 ppm, the sense of smell is disabled at concentrations 100–200 ppm, making it impossible to detect the compound. Rapid death ensues from exposure to more than about 1000 ppm H_2S due to asphyxiation [10, 11]. This means that transformations of sulfur compounds in the water environment must be considered while treating ash-water suspensions and ash transportation waters.

Atmospheric emissions of CO_2 originating from the Estonian oil shale are also a serious problem. A possible solution to reducing the negative environmental impact of emissions is CO_2 mineralization, so-called direct or indirect aqueous carbonation, which leads to abatement of CO_2 emissions (CO_2 binding potential is 200–250 kg CO_2/t OSA) as well as utilisation of OSA for precipitated calcium carbonate (PCC) production [4, 6, 12–14]. While the carbonation leads to changes of pH values of suspension the aim of current study was to investigate the transformations of sulfur compounds in the course of leaching (in anaerobic and aerobic environment) and aqueous carbonation of OSA (and CaS as a model compound) in order to bring out the environmental issues related to possible emissions of toxic H_2S .

2 Materials and methods

In this study two types of model systems (OSA – water and CaS – water), in anaerobic (N_2) and aerobic (in air) conditions were investigated. The aim of aerobic conditions was to imitate the situation in the nature in case of open system, and there is air oxygen access to the suspension. The aim of anaerobic conditions was to imitate the same situation without the access of air oxygen, which takes place in the deeper layers of ash piles. $\text{CaS-H}_2\text{O}$ systems were used as a model in order to explain and simplify the CaS transformations taking place

in OSA-water system. Selected fraction of circulating fluidized bed combustion bottom ash (FBCA) collected from boilers at Estonian power plants was used in the present research. The main characteristics of OSA-s (FBCA and pulverized firing bottom ash (PFA)) [4, 12] including different sulfur forms are presented in table 1. Total sulfur and its bonding forms (sulfide sulfur, sulfate sulfur) in OSA-s were determined according to the Estonian standard EVS 664:1995 for solid fuels [15]. Pure (99.9%) CaS were supplied by Alfa Aesar (German).

Table 1: The main characteristics of OSA-s.

Ash type	(% of dry matter)						Particle mean diameter (μm)	Density (g/cm^3)	BET surface area (m^2/g)
	S _{tot}	S _{sulfide}	S _{sulfate}	CaO _{tot}	CaO _{fr}	CO ₂			
FBCA	5.08	0.28	4.80	53.2	19.7	12.7	26.5	-	1.76
PFA	1.17	0.05	1.12	57.2	30.0	8.3	250.0	2.83	5.26

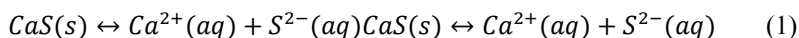
In this context, there was focused on sulfur compounds, therefore, for further experiments were used FBCA. Equilibrium experiments were carried out in a laboratory-scale batch reactor with volume 800 ml using ash-millipore water suspensions by solid/liquid mass ratio 1/10. CaS suspensions concentrations were as follow (in g/L): 0.13, 0.25, 0.5, 1.5 and 2.8. Suspensions were well-mixed at room temperature and atmospheric pressure for 180 min., which was considered sufficient to reach equilibrium. The suspensions were preserved for 24 hours to monitor the behavior of the components for a longer time period. The dynamics of Ca²⁺, OH⁻, S²⁻, SO₄²⁻ and SO₃²⁻ -ions was followed during 15-1440 min. Samples were taken with syringe and filtrated (0.45 μm). The filtrate was analyzed for SO₄²⁻, S²⁻, SO₃²⁻ (using a Lovibond Spectro Direct spectrophotometer), Ca²⁺ (titrimetric method ISO 6058:1984) and OH⁻ (titrimetric method ISO 9963-1:1994 (E)). pH (Mettler Toledo GWb SG2) in the reactor were continuously monitored. Aqueous carbonation was carried out in a 100 ml glass filter absorber using CO₂ containing model gas (15% CO₂ in air, which imitates the CO₂ concentration in actual flue gases). Gas phase composition (H₂S, O₂, CO₂, SO₂, using flue gas analyzer Testo 350-S/-XL) and suspension pH were continuously monitored during the experiments. Suspensions were filtered and the solid residue phase was dried at 105°C. The solid phases were analyzed for chemical composition (free CaO content (ethyleneglycol method) and CO₂ (ISO-10694, ASTM E 191597, DIN EN 13137)).

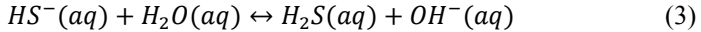
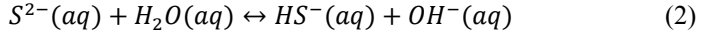
3 Results and discussion

3.1 L Transformations in FBCA – water and CaS – water systems

3.1.1 Anaerobic conditions

Solid CaS dissolves in the water and dissociates (eqn. (1)) to give sulfide ions which will hydrolyze and form hydroxide ions as a result (eqns. (2) and (3)).





In the anaerobic systems of CaS – water the liquid phase contains mainly Ca^{2+} , HS^{-} (main sulfide form in the present pH [9]), and OH^{-} - ions. When OSA is immersed into water, dissociation of forming portlandite ($Ca(OH)_2$), eqn. (8) and dissolution of different salts (anhydrite, gypsum, calcite, dolomite, periclase) occur [14]. During the first minutes of CaS – water and FBCA – water contact, the solution becomes deeply alkaline (~ 11.4 and ~ 12.7 , accordingly) and the pH stabilizes at these values, fig.1. The equilibrium is reached more rapidly in case of FBCA– H_2O system. The pH of aqueous suspensions falls only a few units under anaerobic conditions. This is due to oxidation of sulfide ions, eqns. (4), (5) and (6) or the H_2S evaporation into the gas phase, eqn. (7).

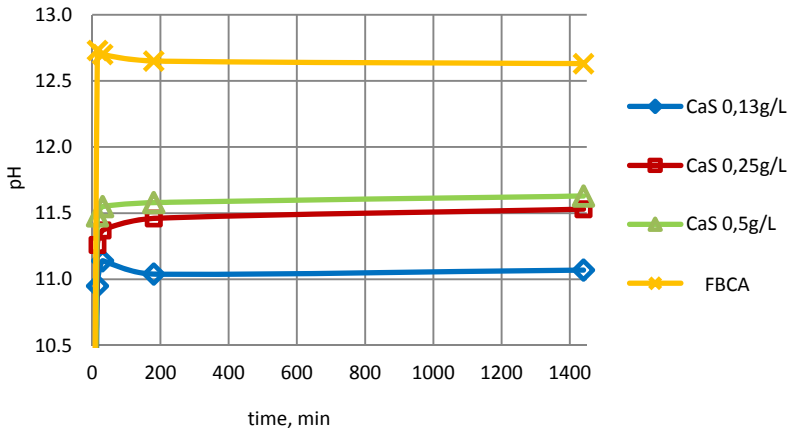
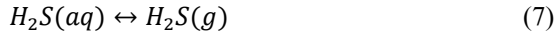
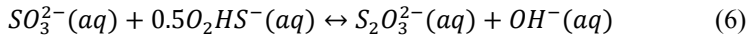
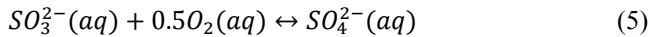
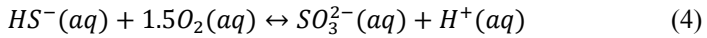


Figure 1: Changes in the pH in CaS– H_2O and FBCA– H_2O systems under anaerobic conditions.

The oxidation of sulfides promotes pH decrease in the system, as the sulphates are weaker bases than the sulfides. Until there is sufficient amount of solid phase, the oxidation of sulfides does not affect the pH of the solution, as oxidized ions are replaced by the dissociation of CaS. The greater amount of initial CaS added into the water the greater the concentration of sulfides in the liquid phase. In contrast to aqueous suspensions of CaS the concentration of S^{2-} ions in aqueous phase kept growing continuously in case of FBCA. Sulfide ion

diffusion from the solid FBCA particle was slower and the equilibrium was not achieved within 24 hours, fig. 2. The content of sulphate ions in the liquid phase increased rapidly >1000 mg/L in case of FBCA – water system and stabilized after 3 hours (180 minutes). In case of the CaS suspensions the content SO_4^{2-} -ions increased steadily from 2 to 23 mg/L (CaS 0.5g/L) during 24 hours, fig. 3 due to leakages in the air-tight system, thus promoting the formation of sulfates. Sulfites content in FBCA leachates was lower compared to CaS, fig. 4. Sulfites were probably formed during the analysis.

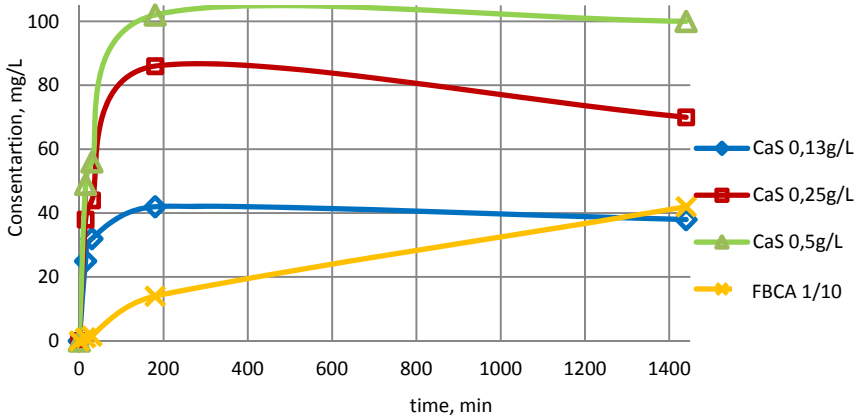


Figure 2: Changes in S^{2-} -ion concentration in CaS–H₂O and FBCA–H₂O systems under anaerobic conditions.

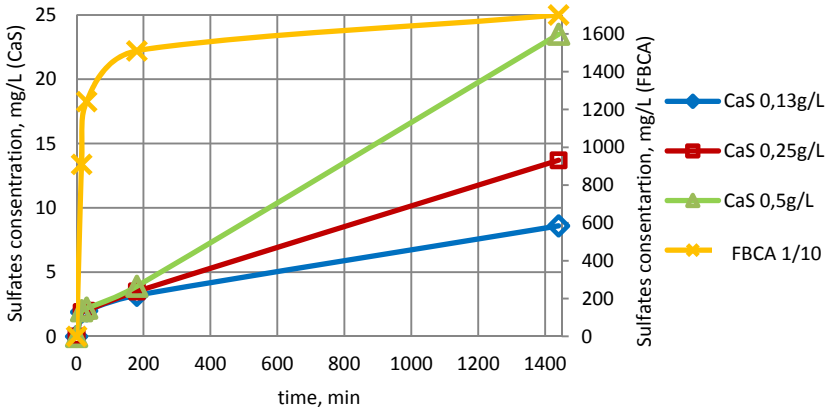


Figure 3: Changes in SO_4^{2-} -ion concentration in CaS–H₂O and FBCA–H₂O systems under anaerobic conditions.

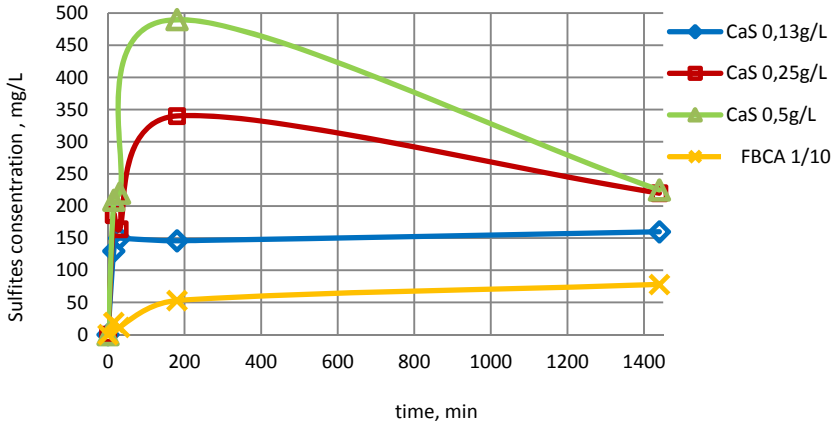


Figure 4: Changes in SO_3^{2-} -ion concentration in CaS–H₂O and FBCA–H₂O systems under anaerobic conditions.

3.1.2 Aerobic conditions

After dissociation of CaS the resulting sulfides bound protons in water so rapidly that the oxidation of solid phase is almost non-existent [9]. The results showed that the majority of sulfides oxidized to sulfites, and reduced sulfates. The aqueous suspensions could include polysulfides and thiosulfates which were not determined in this study; the latter may affects the results. In aerobic conditions the pH of the ash leachates increased higher more rapidly as compared CaS-water systems, fig. 5.

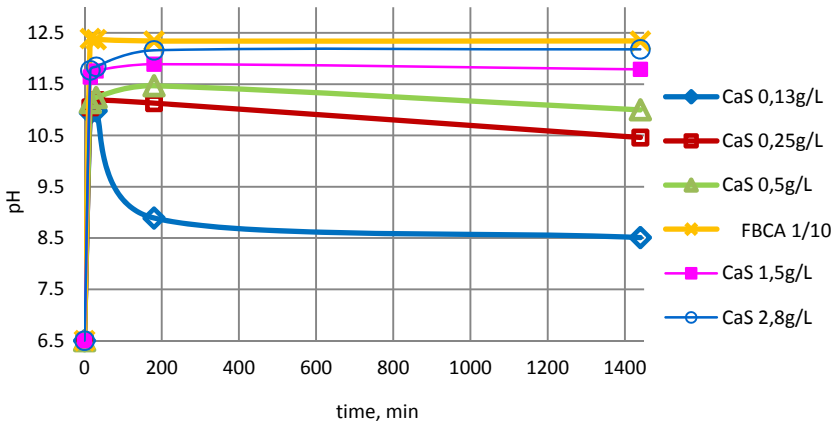
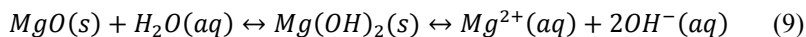
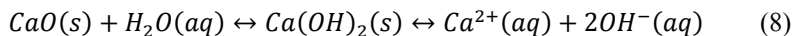


Figure 5: Changes in the pH in CaS–H₂O and FBCA–H₂O systems under aerobic conditions.



Thus, the formation of Ca and Mg hydroxides as well as dissolution, eqn. (8) and (9) was faster than the dissociation of CaS to cations and anions, eqn. (1), and following reaction between sulfides and protons, eqn. (2) and (3).



In case of lower CaS concentrations ($\text{CaS} < 1.5\text{g/L}$) the dissociation of CaS was complete, during the 30 minute of CaS – water contact, so desorption and oxidation of sulfides could not be replaced on account of solid CaS and the system's pH decreases due to absorption O_2 and CO_2 . At higher concentrations ($\text{CaS} > 1.5\text{g/L}$) the system reaches equilibrium and subsequent processes are slow. In FBCA – water system, within 24 hours, the concentration of S^{2-} , SO_4^{2-} and SO_3^{2-} -ions increase steadily, fig. 6, 7 and 8. Thus, after 24 hours of leaching the source of sulfides still remains. Days after, at lower concentrations ($\text{CaS} < 0.5\text{g/L}$), the equilibrium was achieved and sulfites are partially oxidized to sulfates, fig.7 and 8. Diffusion of sulfides from the ash particle into solution took much more time as compared to pure CaS. In FBCA– H_2O system the sulfates had already reached equilibrium after 3rd hour of leaching, as in case of CaS– H_2O systems the concentration of sulfates in the liquid phase kept increasing, fig. 7. Diffusion of sulfates from ash was faster than the oxidation of sulfides to sulfates. Fewer sulfides formed into FBCA - H_2O system than into CaS– H_2O system. Similarly to sulfides (fig. 6), due to oxidation of the latter, the content sulfites increases, fig. 8. Share of sulfites transform to sulfates, depending on the diffusion of sulfides into liquid phase.

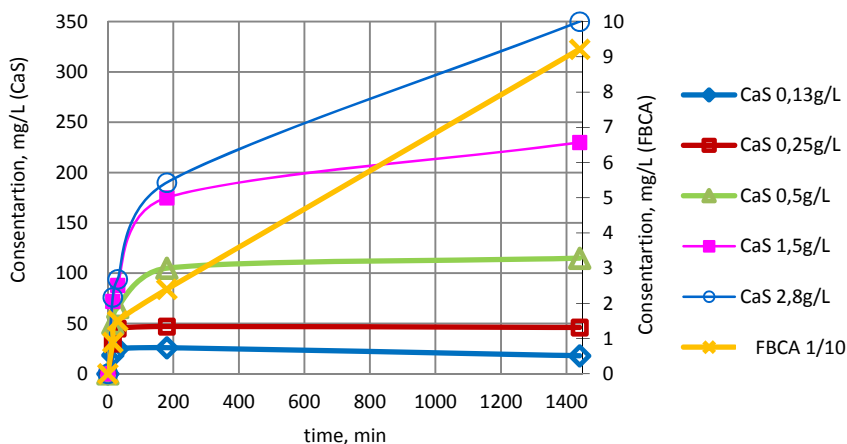


Figure 6: Changes in S^{2-} -ion concentration in CaS– H_2O and FBCA– H_2O systems under aerobic conditions.

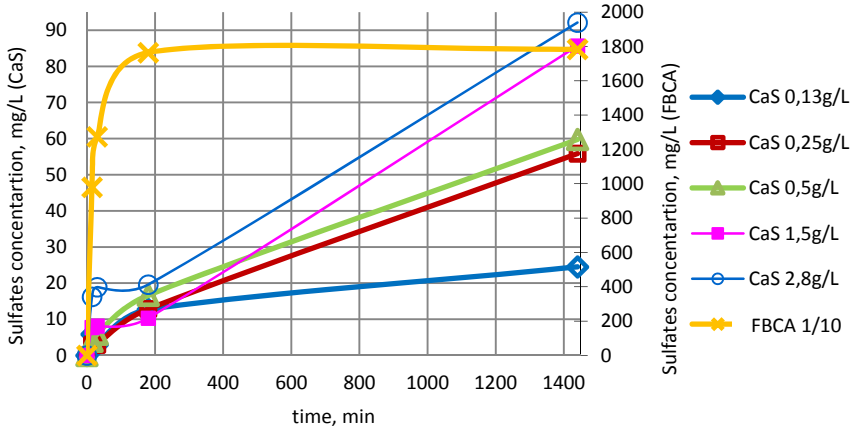


Figure 7: Changes in SO₄²⁻-ion concentration in CaS–H₂O and FBCA–H₂O systems under aerobic conditions.

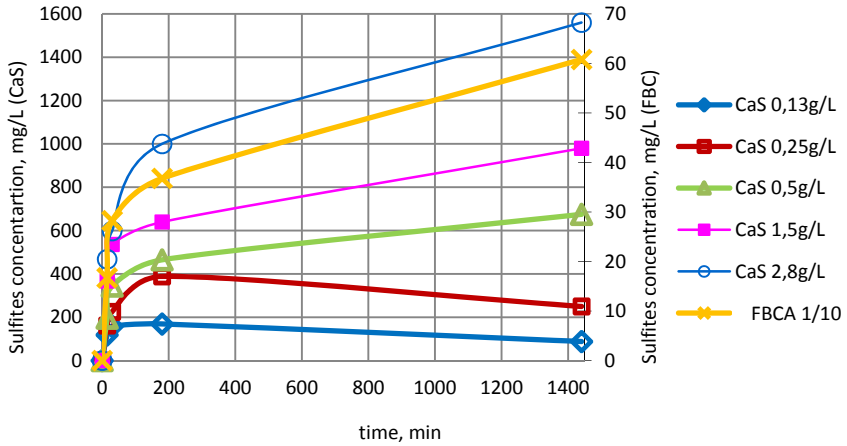


Figure 8: Changes in SO₃²⁻-ion concentration in CaS–H₂O and FBCA–H₂O systems under aerobic conditions.

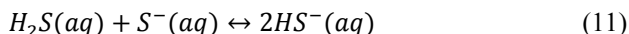
3.1.3 Comparison of the results in anaerobic and aerobic conditions

In both aerobic and anaerobic conditions the aqueous solutions became rapidly highly alkaline after the contact of ash and water, the pH remained stable upon the arrival of the equilibrium, fig. 1 and fig. 5. Thus, proton capture of sulfides, releasing OH⁻ -ions into solution, eqn. (2) and (3), is preferred as compared to the oxidation of sulfides, eqn. (4-6).

In aerobic conditions (CaS<1.5g/L) than equilibrium, pH of the solution falls within 24 hours. Under anaerobic condition at higher CaS concentrations (CaS>0.13g/L) the suspension liquid phase contained ~ twice as much OH⁻ -ions



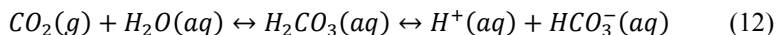
(~4mmol/L) as compared to Ca^{2+} -ions (~2mmol/L), as result of H_2S in the solution which leads to the additional metallic sulfide dissolution according to eqn. (11):



Therefore, more hydrogen sulfide ions would be provided into solution and for equilibrium constants to remain the hydrogen sulfide ions have to bind more protons, resulting formation of H_2S and remaining of more hydrogen ions in the solution. In case of anaerobic conditions the sulfides content in the liquid phase was lower, fig. 2, 5. Thus, the oxidation of sulfur compounds accelerates the dissolution of CaS. Although H_2S releasing in gaseous form has an important role in solid phase dissociation, the slower dissociation of CaS was determined in anaerobic conditions. Desorption of H_2S was suppressed in the presence of oxidants. Under aerobic conditions Ca^{2+} -ions content decreased, table 2, thus in oxidizing condition due to binding of the Ca^{2+} -ions (eqn. (8) and (13)), the solidification was beneficiary. Therefore contrary to the sulfides, the concentration of SO_4^{2-} -ions was in every case higher under aerobic conditions fig. 3 and 7.

3.2 Aqueous carbonation of FBCA and CaS

Carbonation experiments showed that small amounts of H_2S were emitted already in the region of high pH value (pH~12) during the first minutes of carbonation process, fig. 9. The system pH decreases as model gas was bubbled through the aqueous suspensions of FBCA or CaS. CO_2 behaves as acid in the aqueous systems [14], eqn. (12):



During carbonation, in case of CaS– H_2O system, pH decreases faster and to lower values, than in FBCA– H_2O system, fig. 9. In case of CaS the pH reached equilibrium (pH~6.3) in 5 minutes, as in case of FBCA system in 30 minutes (pH~6.8). In FBCA system pH stayed on a high level until almost all free lime (CaO) was utilized (as long as calcium was carbonated). In CaS– H_2O system the pH decreased rapidly because of lack of CaO. pH decrease favors the evaporation of H_2S , which also earlier studies refer [14]. When the suspension pH decreased below 7.5, the content of H_2S in off-gas reached 110 ppm in case of FBCA and >1500 ppm in case of CaS (CaS 0.6g/L). Release of the H_2S stopped in correlation with the respective source of sulfide. Thus, at pH values <10 desorption of gaseous H_2S is preferred to oxidation of sulfides, which was expressed by the intense emission of H_2S . Determination of solid phase composition indicated that over 85% of free lime (content of free CaO <2%) was utilized before reaching into the intensive H_2S_g emission region (pH<9) during aqueous carbonation of OSA. The amount of CO_2 bound was 210kg CO_2/t FBCA.

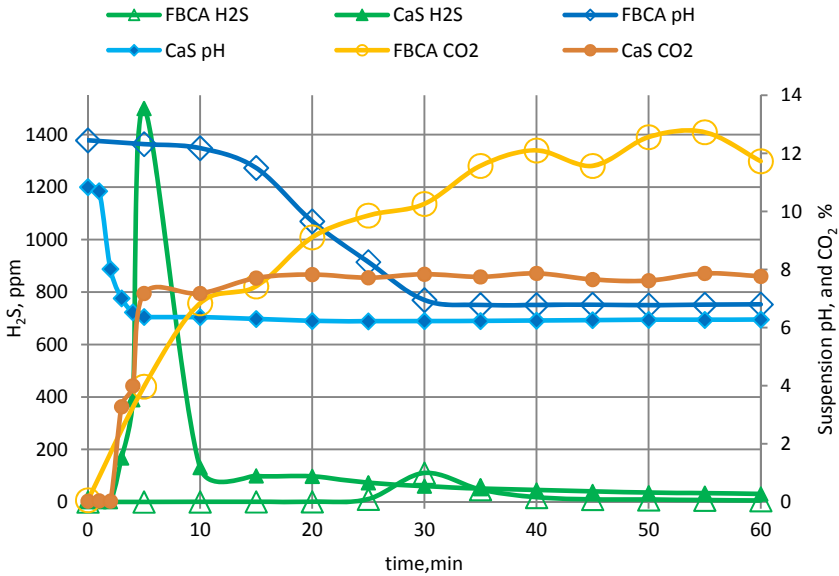


Figure 9: Changes in the composition of off-gas and suspension pH during aqueous carbonation of FBCA.

4 Conclusions

Experiments in model systems showed that transformations of the sulfur compounds in the water environment must be considered while using hydrotransport and open air deposition of oil shale ash as well as treating alkaline ash transportation waters. H₂S has an important role in CaS dissociation. As long as there is a solid CaS in the system, the source of sulfides, O₂ and CO₂ absorption does not affect the oxidation of sulfides and suspensions pH decrease. The kinetic desorption of gaseous H₂S(g) is preferred to oxidation of sulfides when suspension pH < 10. Taking environmental problems into consideration, the pH of the aqueous carbonation system of OSA must be monitored – the separation of highly toxic gaseous H₂S(g) can be minimized by optimizing pH value of the system. Carbonation should be discontinued at the time when no more CO₂ is committed by the amount of free CaO in the OSA, thus preventing a rapid pH decrease of the system.

Acknowledgements

The financial support of Estonian Ministry of Education and Research (SF0140082s08), Estonian Science Foundation (Grant 9334) and Graduate School "Functional materials and technologies" is gratefully acknowledged.



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