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## Equilibrium calculations in aqueous carbonation of oil shale waste-sulfur compounds

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The main energy source in the Republic of Estonia is the local fossil fuel - oil shale (OS) - which is used for the power as well as shale oil (SO) production. As a consequence, large quantities of OS mineral waste (~8.2 million tons of OS waste per 2012) from the combustion processes accompanied by gaseous emissions of $CO_2$, $SO_x$ and $NO_x$ (11.7 million tons, 32 and 10 thousand tons per 2012 according to the Eesti Energia AS and the Viru Keemia Grupp AS) are produced. The European Union is constantly introducing stricter conditions for the emissions of greenhouse gases (GHG) and other harmful pollutants as well as new initiatives for environmental technology, waste recovery and recycling, affecting also the OS sector in Estonia (e.g. the goal is to reduce GHG emissions by 20-30% and annual $SO_2$ emissions to 25 thousand tons by 2020, which is 2.5 times lower than the initially allowed amount). The distribution of sulphur between gaseous and solid phases depends on the OS combustion technology (the concentration of $SO_2$ in circulating fluidised bed combustion flue gas is on the level of some ppm). Sulfur (<2% in Estonian OS) remains in the OS power plant ashes mainly as sulfates (4.8 wt%), but also as sulfides (0.28 wt%), and in the solid waste of SO production mainly as sulfides (4.6 wt%) and little as sulfates (0.36 wt%) (the percentages corresponds to the contents of the OS waste, which in this study were used). Depending on the amount of sulfides and oxidants in the aqueous system, the pH drop could induce the release of highly toxic gaseous H2S. In order to minimize the environmental risks accompanied by utilizing OS wastes as a $CO_2$ trap (up to 290 kg-$CO_2$/t-OS ash) and/or cheap Ca-source for PCC production the routes of sulfur compounds transformations have to be explored in different conditions. The current study was focused on the direct aqueous (S/L=1/5 to 1/250) carbonation of OS wastes, such as circulating fluidized bed ash (CFBCA) from power production and solid heat carrier ash (SHCA) from SO production. The model systems were studied by thermodynamic equilibrium calculations using HSC Chemistry 7.1 version software. The aim was to imitate the real processes (based on the previous experiments) which occur during the aqueous carbonation of OS wastes, to study the complex equilibrium of sulfur species under different oxidation conditions (model system 1 – 15 % $CO_2$ in air and model system 2 – 14.6 % $CO_2$ and 0.5 % $SO_x$ in air, at 25°C and 1atm) and predict the optimum conditions for the $CO_2$(g) binding. The equilibrium calculations allowed to evaluate the theoretical binding capacity of $CO_2$(g) OS wastes. The aqueous suspension of SHCA had almost twice the binding potential (600 - 700 mol/$m^3$, 264 – 308 kg-$CO_2$/t) of power plant ash CFBCA (400 - 450 mol/$m^3$, 176 - 198 kg-$CO_2$/t). The theoretical $CO_2$ binding potential depended on the competitive $SO_x$ content in the flue gas (model system 2); the S/L ratio of the system had no influence. The HSC calculation results of model systems pH (11.28 → 7.5 SHCA; 10.5 → 6.8 CFBCA) were in reasonable accordance with the experimental results (12.28 → 7.5 SHCA; 12 → 6.8 CFBCA) of aqueous carbonisation end-points. The initial pH varied more, because the untreated ashes are thermodynamically more unstable and unlike the experiments, the state of equilibrium calculations indicates infinite time. Contacting OS wastes with water produced highly alkaline leachates saturated with $Ca^{2+}$-ions. After all free lime as well as MgO was realised by $CO_2$, the system pH and the concentration of $Ca^{2+}$-ions decreased appreciably. The Ca-(Mg)-silicates decomposed in acidic conditions releasing Mg2+-ions into the solution. In case of the system 2 the $SO_x$ compounds promoted oxidation and the system pH decreased even further. As the sulfuric acid is stronger than carbonic acid, the percentage of $SO_4^{2-}$ and $HSO_4^{-}$-ions was elevated. The equilibriums of sulfide species ($S_2^{-}$, $HS^{-}$, $H_2S(aq)$ and $H_2S(g)$) were dependent of the system pH. $HS^{-}$-ion dominated in all systems. As the suspension pH decreased below 10 the concentration of $H_2S(g)$ increased reaching the same level of $HS^{-}$ ions (pH ~9.5 and ~8.5, accordingly in model system 1 and 2). $H_2S(aq)$ changed similarly but maintained at lower values. The SHCA systems showed clearly, that when all available Ca species were used for $CaCO_3$ formation (including CaS as the main source of aqueous and gaseous sulfide species) the content of sulfides was also depleted. In case of model system 1 the concentration of sulfide species achieved minimum (10-36 mol/L the lowest value set by HSC software) at pH <10 and in model system 2 at pH <9. Even very small amounts of model flue gas provoked the oxidation of sulfides to sulfur intermediate oxidation forms ($S_xO_y^{2-}$ and $SO_3^{2-}$) and sulfates. As the systems reached to the maximal $CO_2$ binding potential, all the solid $CaSO_4$ forms decomposed releasing $SO_4^{2-}$ and $HSO_4^{-}$-ions into the liquid phase. The growth of the content of carbonates stabilised after achieving the maximum carbonation potential ($CaCO_3$ dominates in all systems). In case of the model system 2, the concentrations of carbonates started to gradually decline, due to progressing sulfation. Considering the amounts of deposited waste from OS sector, the mineral carbonation of acidic gases is a promising solution in reducing greenhouse gas emissions and utilizing OS waste, while monitoring the pH and oxidation potential of aqueous carbonation to minimise sulfur pollution.

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Page 40