

Thermodynamic analysis of possibility of using calcium compounds for removal of heavy metal ions from aqueous solutions

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Abstract. The aim of this investigation is the thermodynamic simulation of processes, occurring at interaction of calcium compounds (silicates etc.) with water solutions containing heavy metals, as well as the analysis of the obtained results by explanation of the effects observed in the binding and immobilization of heavy metal ions from water solutions. The results of the thermodynamic modelling allowed the authors to make a number of conclusions that are converged with the literature experimental data. In particular, the main components of the cement clinker during the contact with water allow reaching the high pH value of the water medium. This is sufficient to convert most heavy metal ions into insoluble compounds. The processes, occurring during the interaction of calcium compounds with water and dissolved heavy metals, in the case of equilibrium achieving, should lead to a significant decrease in the concentration of heavy metals in water. These processes should be accompanied by the increase in the concentration of calcium ions in the solution. The presence of carbon dioxide in excess in the system leads to the fact that the solution pH will correspond to a neutral or weakly acidic medium. However, even in this case, there will be a decrease in the concentration of heavy metal ions by several orders of magnitude.

1. Introduction

The possibilities of using calcium silicates and calcium aluminates for binding and immobilization of toxic heavy metals from industrial acid discharge are described in the scientific literature. For this aim objectives, it is proposed to use a cement or a cement clinker [1-9], as well as some types of metallurgical slag containing a large number of calcium silicates and calcium aluminates [10-18]. By nowadays, a large amount of experimental data on the effectiveness of such processes has been accumulated. At the same time, the mechanism for binding of heavy metal ions by phases based on calcium silicates and calcium aluminates still are not sufficiently investigated, that impedes the development of wastewater treatment methods by means of such phases, which would be characterized by stable efficiency.



The aim of this investigation is thermodynamic simulation of the processes occurring at interaction of calcium compounds (silicates, aluminate and also, for comparison, calcium oxide) with water solutions containing heavy metals, as well as the analysis of the obtained results by explanation of the effects observed in the binding and immobilization of heavy metal ions from water solutions.

2. Methods

In the modelling process the capabilities of the software complex "FactSage" (version 7.0) were used [19-20]. "Equilib" module and "FThelg" thermodynamic database (database for modelling of water solutions and water containing in solid phases, version 2015) were used. Data for some substances and phases of variable composition were also taken from the "FToxid" database (database for modelling of oxide systems, version 2015). For modelling of water solution "FThelg-AQDD" phase data were used, which is due to the extended equation of Debye-Huckel allows with sufficient accuracy to describe solutions with a relatively high concentration of solutes. The simulation was performed for a temperature of 20 °C and a pressure of 1 bar.

Calculations were performed for 1 kg of water, where up to 5 g of the substance from the following list were added: Ca_3SiO_5 (alit), Ca_2SiO_4 (belit), tricalcium aluminate $\text{Ca}_3\text{Al}_2\text{O}_6$ (these three substances are the basis of cement clinker, as well as frequent components of slag, for which there is data on their high sorption capacity with respect to heavy metals). In addition, the simulation was performed for cases when CaSiO_3 , CaO and SiO_2 are added to the water.

Modelling was carried out for the cases when these substances are added to pure water (Figure 1), in aqueous solution (Figures 2-4), containing 1 gram of salts (chlorides) of heavy metals (copper and lead are such metals), as well as for systems that include in addition to 1000 g of water, 1 g of heavy metal chloride and additives from the list above of 5 g of carbon dioxide (Figures 5-9). Interest in the last group of systems is the fact that the solutions have a high pH value (this value is provided by these additives) in the open air. These solutions will absorb carbon dioxide. It will lead to a decrease in the pH of the solutions and the concentration of calcium ions. In this case, it is necessary to assess whether the associated heavy metal ions will be released.

3. Results and discussion

On Figures 1-9 some of the most interesting results of the simulation are presented. The results are presented in the form of pH dependencies of the water phase, the concentrations of calcium, copper and lead, as well as the mass of the solid phase in equilibrium with the water medium (and separately the masses of calcium carbonate) with the mass of the substance added to 1000 g of water from the list above. The simulations showed that the addition of SiO_2 has practically no effect on the medium pH and it does not bind the heavy metal ions. Therefore, the data for this substance are presented only in Figure 1 for comparison with the rest.

Analysing the presented simulation results, it should be taken into account that they are obtained for the case of achievement of the chemical equilibrium by the studied systems without taking into account any kinetic factors. Nevertheless, the following main conclusions can be drawn, which are useful in terms of understanding the mechanism of immobilization of heavy metals present in water:

The main components of the cement clinker during the contact with water allow to reach the pH value of the water medium of the order 12. This is slightly lower than the value for CaO and slightly higher than for CaSiO_3 . In the real system, such a pH value is possible only in the water layer directly reacting with the additive, but this is also sufficient to transfer most of the heavy metal ions into insoluble compounds (hydroxides, etc.).

The processes occurring during the interaction of calcium compounds with water and dissolved heavy metals lead to a significant decrease in the concentration of heavy metals (for the studied systems the concentration of heavy metal, according to the simulation results, decreases from 2 to 5-6 orders under applied conditions).

The same processes lead to reaching of the equilibrium concentration of calcium ions in the solutions in the order of 0.01-0.02 wt. %.

The presence of CO_2 in excess in the systems leads to the fact that the solution pH will correspond to a neutral or weakly acidic medium. However, in this case, there will be a decrease in the concentration of heavy metals ions by several orders of magnitude. Insoluble phases, immobilizing the heavy metals, will be largely composed of carbonates and hydroxocarbonates. It should be especially noted that starting from a certain mass threshold of the additive calcium carbonate becomes the main solid product of interaction in the studied systems, which is practically not formed at the stage of binding of heavy metals ions.

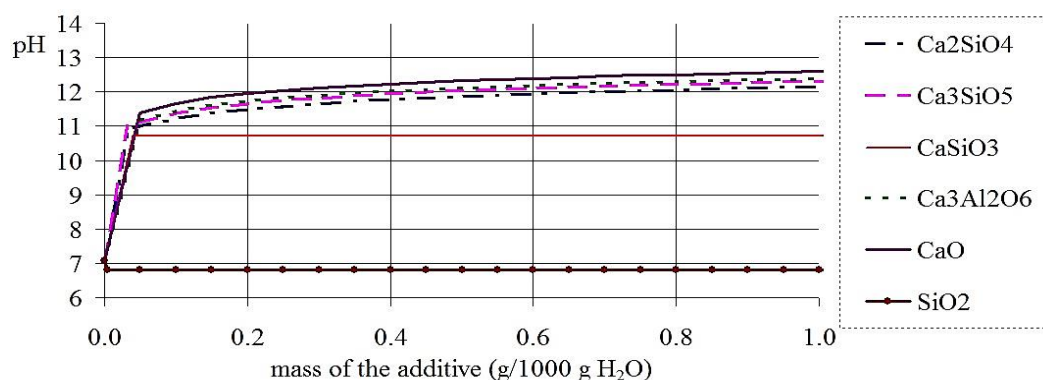


Figure 1. The dependence of medium pH from the mass of the additive (for the mass range 0-1 g per 1000 g of water).

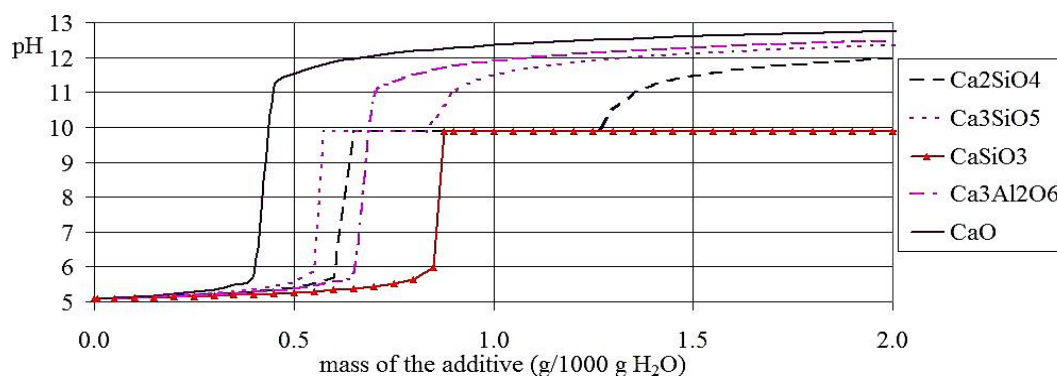


Figure 2. The dependence of medium pH, which includes 1 g of CuCl_2 per 1000 g of water, from the mass of the additive (for the mass range 0-2.0 g per 1000 g of water).

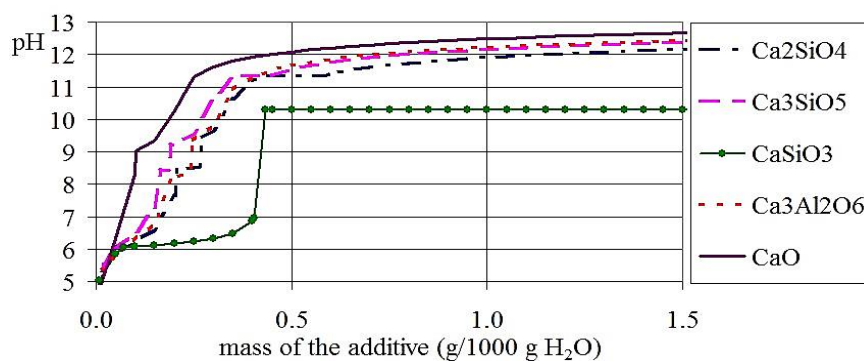


Figure 3. The dependence of the medium pH, that includes 1g of PbCl_2 per 1000 g of water, from the mass of the additive (for the mass range of 0-1.5 g per 1000 g of water).

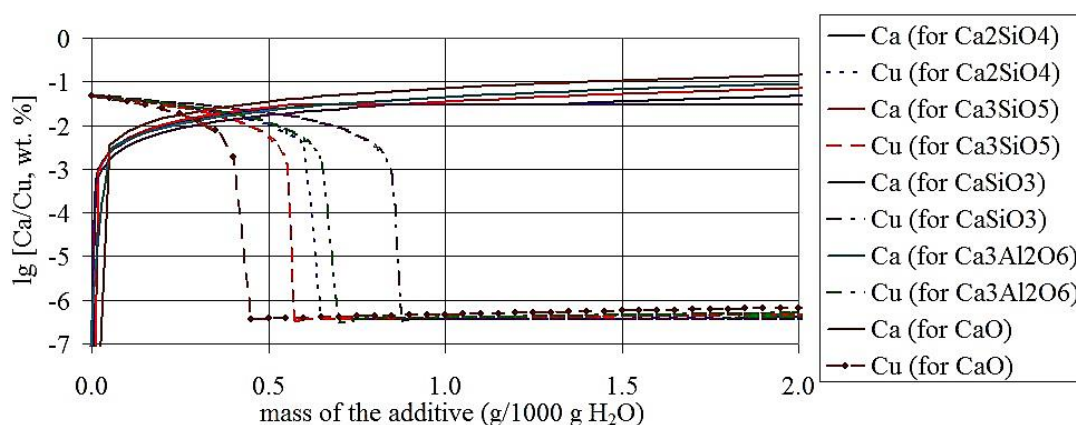


Figure 4. The dependence of the calcium and copper content in the solution (for the system that includes 1 g of CuCl_2 per 1000 g of water) from the mass of the additive (for the mass range 0-2.0 g per 1000 g of water).

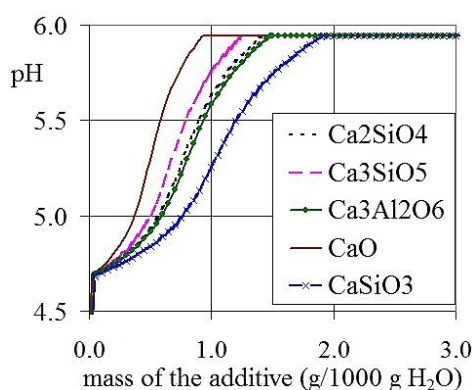


Figure 5. The dependence of the medium PH, including 1 g of CuCl_2 and 5 g of CO_2 per 1000 g of water, from the mass of the additive (for the mass range of 0-3 g per 1000 g of water).

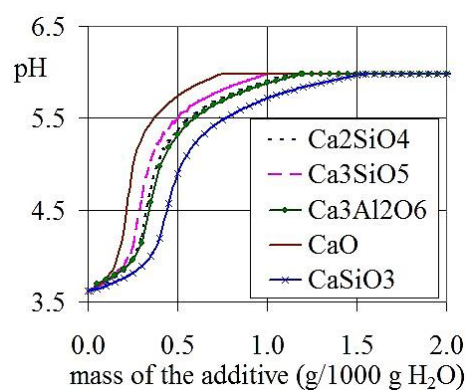


Figure 6. The dependence of the medium PH, including 1 g. PbCl_2 and 5 g of CO_2 per 1000 g of water, the mass of the additive (for the mass range 0-2 g per 1000 g of water).

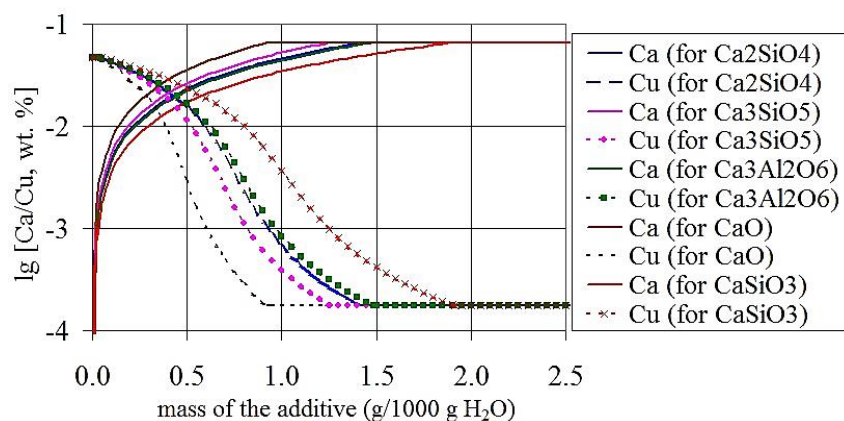


Figure 7. The dependence of calcium and copper content in the solution (for a system that includes 1 g of CuCl_2 and 5 g of CO_2 per 1000 g of water) from the mass of the additive (for the mass range of 0-2.5 g per 1000 g of water).

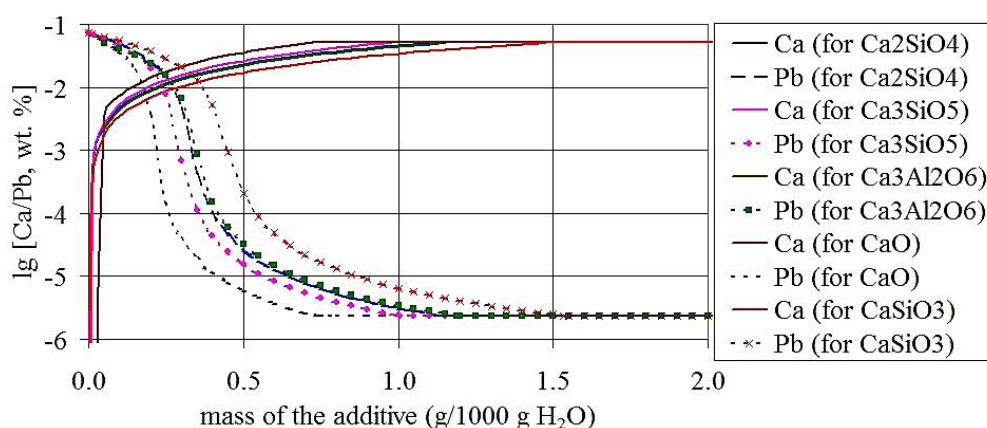


Figure 8. The dependence of calcium and copper content in the solution (for a system including 1 g PbCl_2 and 5 g CO_2 per 1000 g water) from the mass of the additive (for the mass range 0-2 g per 1000 g water).

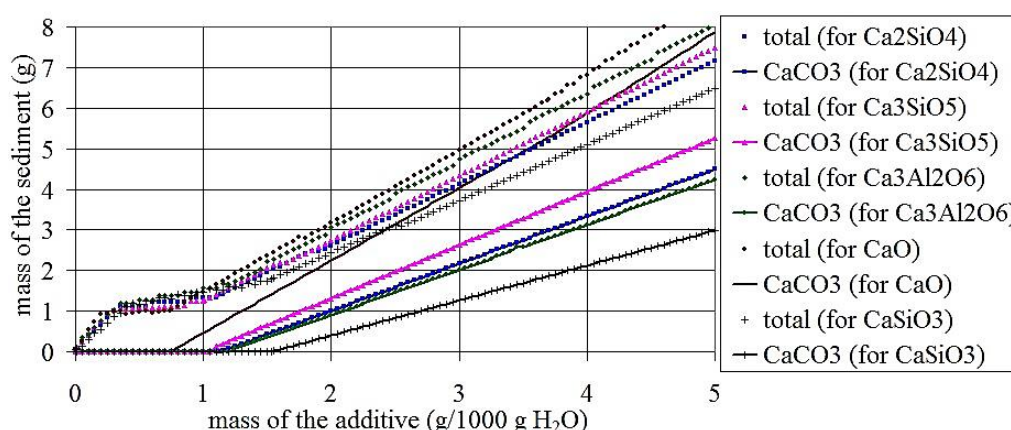


Figure 9. The dependence of the solid phases masses and calcium carbonate separately for a system, including 1 g PbCl_2 and 5 g of CO_2 per 1000 g of water, from the mass of the additive (for the mass range of 0-5 g per 1000 g of water).

In the present conditions, the phases containing calcium silicates and calcium aluminates for the binding and immobilization of toxic heavy metals in industrial discharge, this can lead to a situation where formed insoluble in water phases, containing heavy metals, will be isolated from the water environment by a layer of calcium carbonate. It will help to prevent the return of heavy non-ferrous metals into the water.

4. Conclusion

The results of the thermodynamic modelling allowed to make a number of conclusions that are converged with the literature experimental data. These conclusions are useful for understanding the mechanism of heavy metals immobilization by calcium silicates and calcium aluminates, contained in some metallurgical slag and cement clinker.

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