

## **Summary of the Ph.D. thesis**

### *Mineral waste raw materials as potential SO<sub>2</sub> sorbents for flue gas desulfurization systems in the power industry*

The power sector uses almost exclusively high-quality limestone as SO<sub>2</sub> sorbent. Due to the depletion of limestone resources with appropriate parameters and the successive tightening of SO<sub>2</sub> emission limits, it is necessary to conduct research on the use of other carbonate raw materials.

The main objective of the doctoral thesis was to determine the parameters affecting the efficiency of the SO<sub>2</sub> sorption process and the impact of chemical modifications on this process in conditions corresponding to the fluidized bed combustion technology.

The research material contains rock samples of limestones, dolomites and magnesites. They were originated from mineral waste stored in heaps and raw materials extracted from deposits, the processing of which leads to the formation of fractions with limited development possibilities.

This work is a response to the needs of the power industry and rock raw materials while considering the requirements of environmental protection in terms of SO<sub>2</sub> emissions and the management of mineral tailings and processing waste.

The assessment of sorption properties of the investigated carbonate rocks was carried out by laboratory scale experiments respecting guidelines of the Ahlstrom Pyropower Development Laboratory in specially engineered equipment. The determination of parameters affecting the efficiency of SO<sub>2</sub> sorption required the study of natural rock samples and products of the decarbonization/desulfurization stages.

The results clearly showed that the high content of carbonate component in the sorbent does not guarantee the high efficiency of SO<sub>2</sub> sorption. The effective porosity and specific pores distribution after decarbonization play a key role in SO<sub>2</sub> sorption. Effective porosity serves as evacuation of CO<sub>2</sub> by diffusion paths during decarbonization in the same time allowing for SO<sub>2</sub> penetration into grains and sorption. The contribution of meso- and macropores (being effect of decarbonization) is positively correlated with high efficiency of SO<sub>2</sub> sorption, which is the case of the investigated materials. The contribution of micropores into total pore volume of rock and decarbonized samples has a negative impact on the SO<sub>2</sub> sorption. Too small pore diameters cause a rapid build-up of the pore space with sulfate reaction products blocking the access of SO<sub>2</sub> into the sorbent.

It was shown that magnesium oxide, apart from calcium oxide, actively participates in the sorption process. The formation of thermally stable (under fluidized bed combustion conditions) sulfate phases containing calcium and magnesium was experimentally confirmed.

Reactions of MgO with SO<sub>2</sub> lead to the formation of magnesium sulfate (MgSO<sub>4</sub>) and (with the participation of CaO) calcium and magnesium polysulfate (CaMg<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>). Among the studied rocks, dolomites had the best sorption properties. This can be attributed to the two-stage thermal dissociation of dolomite allowing for the formation of favorable parameters of the porous texture. It was also shown that it is possible to improve the sorption properties of limestones by modifying their composition with potassium compounds causing an increase of the pore space during decarbonization. This phenomenon allows for increasing the range of SO<sub>2</sub> infiltration deep into the sorbent grain.

The presented results indicate the validity of continuing research on the use of dolomites and magnesites as effective SO<sub>2</sub> sorbents in fluidized bed combustion. Particularly attractive seems to be the use of carbonate precipitation raw materials as sorbents, which is part of the trend of sustainable development, considering the protection of deposits and waste management in a closed cycle.