STUDIES ON THE WET PROCESS PHOSPHORIC ACID PRODUCTION BY THE DIHYDRATE-HEMIHYDRATE METHOD

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Summary

Phosphoric acid is used in many industrial fields, including chemical, food or pharmaceutical industry and it is considered the second one in terms of the amount used in non-organic industry. Over the past few years, the production of phosphoric acid increased significantly. Due to the continuing global demand, further increase of production volume of phosphoric acid worldwide is projected. The most prevalent production method of this acid is the wet process by dihydrate method, nevertheless, combined methods, such as dihydrate - hemihydrate (DH-HH), hemihydrate - dihydrate (HH-DH) and hemihydrate - dihydrate - hemihydrate (HH-DH-HH) are used more and more often nowadays. It is caused by the need of improving efficiency and productivity of production installations as well as the pursuit to minimize phosphate losses and limit waste production.

The research presented in this work concerns the conversion of dihydrate calcium sulphate into hemihydrate in phosphoric acid solution. The process temperature, content of phosphates, sulphates and impurities in liquid phase and also crystallization of nuclei of hemihydrate calcium sulphate were analysed in terms of their impact on the process. The research was performed on a model system as well as the actual one, with the use of phosphoric acid (EKF) and phosphogypsum from Grupa Azoty Zakłady Chemiczne Police Inc. in case of the latter.

Based on the research performed on the model system, it was found that the level of the conversion of dihydrate calcium sulphate in relation to α-hemihydrate calcium sulphate increases along with the increase of the temperature of the process and/or the higher content of phosphates and/or sulphates in the reaction mixture. The higher temperature of the process was applied, the higher level of recrystallization $CaSO_4 \cdot 2H_2O$ was acquired, with the lower content of phosphates and/or sulphates in phosphoric acid. However, no significant impact of magnesium, aluminium, iron, silica and fluorine ions in the phosphoric acid on the level of conversion $CaSO_4 \cdot 2H_2O$ into α-$CaSO_4 \cdot 0{,}5H_2O$ was found.

The research realised in the actual system confirmed dependencies found during performing experiments in the model system. Also, it allowed to determine a degree of filtration of the received calcium sulphate hydrates.

It was confirmed that performing the process of conversion dihydrate calcium sulphate into α-hemihydrate with the participation of 20% nuclei α-$CaSO_4 \cdot 0{,}5H_2O$ allows to receive approximately 80% higher degree of transformation in proportion to the non-nuclei process, performed in the same conditions. It was also possible to get the degree of the transformation $CaSO_4 \cdot 2H_2O$ into α-$CaSO_4 \cdot 0{,}5H_2O$ within the range of 82,5% – 95,2%, with 40% mass participation of nuclei α-$CaSO_4 \cdot 0{,}5H_2O$ in the assumed process conditions (temperature 92°C, 28% mass P_2O_5 and 4% mass SO_4^{2-} in EKF, time of the reaction mixture inside the reactor - 90 minutes). Significant influence of fluorine, aluminium and silica on the conversion degree of $CaSO_4 \cdot 2H_2O$ into α-$CaSO_4 \cdot 0{,}5H_2O$ and filtration of the received calcium sulphate hydrates.

Due to the performed conversion $CaSO_4 \cdot 2H_2O$ into α-$CaSO_4 \cdot 0{,}5H_2O$, the content of total phosphates dissoluble in ammonium citrate and dissoluble in water in residual sulphate dihydrate was decreased in comparison with the initial phosphogypsum. The degree of transition of specified forms of phosphates from sediment to phosphoric acid was 77%, 84% and 71% respectively, what was directly connected with the increase of concentration P_2O_5 in phosphoric acid about 1 – 3,3% mass. The water content in the sediment was decreasing by about approximately 25% mass to about 11% mass.

The research within the actual system proved that it is possible to perform the conversion process of $CaSO_4 \cdot 2H_2O$ into α-$CaSO_4 \cdot 0{,}5H_2O$ in much milder conditions (4 – 6% mass SO_4^{2-}, temperature 90 – 95°C) than in the classical method DH-HH, where the temperature of 100°C as well as the higher content of sulphates and phosphates (10 – 20% mass H_2SO_4, 20 – 30% mass P_2O_5) are required.

The use of dihydrate - hemihydrate method can significantly influence the process of producing phosphoric acid, causing the increase of phosphate efficiency in the process as well as the increase of the phosphoric acid concentration (less energy, necessary to make the acid more concentrated, is consumed) and also the decrease of the waste amount stored on the dump. Therefore, the negative impact of the phosphoric acid production on the environment will be limited.

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