Kinetics of Conversion of Concentrated Celestite Ore to Acid Strontium Oxalate Monohydrate in Oxalic Acid Solutions

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Extended Abstract

Celestite mineral ($SrSO_4$) is enriched by flotation methods to obtain concentrated celestite ore. $SrCO_3$ is produced industrially from concentrated celestite ore progressively by Direct Carbon Reduction Method or directly by Conversion Method using alkaline sodium carbonate solution. $SrCO_3$ produced from $SrSO_4$ is used for the production of strontium metal or its compounds.

It is possible to obtain alkaline free product by conversion of $SrSO_4$ to $SrCO_3$ progressively first by hydrometallurgical and then by pyrometallurgical methods using oxalic acid solutions. The effects of stirring speed, concentration of reactive compound in the solution, temperature and particle size of concentrated celestite ore were investigated using 2 g of concentrated celestite ore, 301.5, 313, 328, 343 and 358 K temperatures and 1 L solution obtained by dissolving 0.1, 0.2, 0.4, 0.8 and 1.2 mol of $H_2C_2O_4$ to convert $SrSO_4$ to acid strontium oxalate monohydrate ($Sr(HC_2O_4)(C_2O_4)_{0.5} \cdot H_2O$).

$H_2C_2O_4$, H^+, $HC_2O_4^-$ and $C_2O_4^{2-}$ are formed in the solution by dissolving $H_2C_2O_4$ in water. The concentration of $C_2O_4^{2-}$ is the lowest amongst the other ions. Sr and S elements pass to the solution during reaction. The concentration of Sr in the solution is slightly less than that of S. This is due to the presence of Sr in $SrC_2O_4 \cdot H_2O$ product layer that covers the surfaces of $SrSO_4$ particles and the remaining amount is found in the chelate compound $H[Sr(C_2O_4)_{1.5}(H_2O)]$ dissolved in the solution.

The conversion reaction is under chemical reaction control in accordance with the Shrinking Core Model. It was determined that 500 rpm stirring speed was enough to eliminate the resistance of liquid film layer surrounding the solid particles. The conversion of $SrSO_4$ in $H_2C_2O_4$ solutions takes place in two consecutive reaction steps. In the first step, $SrC_2O_4 \cdot H_2O$ and HSO_4^- are formed during the reaction of $SrSO_4$ with $H_2C_2O_4$ in the solution. The formation rate of $SrC_2O_4 \cdot H_2O$ is 0.33[rd] order with respect to $H_2C_2O_4$ concentration with activation energy of 43000 kJ kmol^{-1}. The second step is an equilibrium reaction where water soluble $H[Sr(C_2O_4)_{1.5}(H_2O)]$ is formed during the reaction of $SrC_2O_4 \cdot H_2O$ and $H_2C_2O_4$. When the concentration of $H[Sr(C_2O_4)_{1.5}(H_2O)]$ is reached to its equilibrium value, the conversion reaction stops. The order of the forward reaction rate of the second step varies between 0.31[st] and 0.68[th] with respect to the $H_2C_2O_4$ concentration at increasing temperatures with activation energy of 32740 kJ kmol^{-1}. The order of the reverse reaction rate of the second step is first order with respect to $H[Sr(C_2O_4)_{1.5}(H_2O)]$ concentration with activation energy of 10040 kJ kmol^{-1}. 100 % conversion can be achieved when the highest temperature, highest $H_2C_2O_4$ concentration and lowest particle size of the ore are used. Since, there is no study carried out on this subject in the literature, it is not possible to compare the kinetic parameters obtained in this work.

Quantitative chemical analysis of the concentrated celestite ore and the reactive compounds in the solutions were performed by using XRF and volumetric analysis, respectively. For the phase characterization of the concentrated celestite ore and the solid reaction products, XRD and simultaneous TGA/DTA/MS analytical techniques were utilized.